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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The objective of his AFOSR research program was to work toward developing aluminum cluster-containing materials for propulsion applications. His efforts focused on four distinct approaches: (1) studying covalent aluminum-containing molecules/clusters, especially novel aluminum hydride clusters/molecules, (2) investigating the reactivity of aluminum cluster anions, (3) exploring the possible synthesis of derivatives of aluminum hydride clusters/molecules, and (4) investigating the prospects of making ionic "molecules" composed of cations and aluminum containing cluster anions. The experimental methods included the use of unique sources, mass spectrometry, anion photoelectron spectroscopy, ion cyclotron resonance spectrometry, and bench-top synthesis. He was able to discover whole new categories of previously unknown aluminum hydrides, to show that the reactivity of aluminum cluster anions were governed by spin conservation rules, to synthesize small quantities of aluminum hydride derivatives, and to generate and characterize beams of several novel ionic "molecules"					
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**Final Performance Report**

**Toward the Development of Aluminum Cluster-Containing  
Materials for Propulsion Applications**

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The objective of our AFOSR program was and is to work toward the development of aluminum cluster-containing materials for propulsion applications. This constitutes the Final Report for our first cycle of funding under grant award number, ~~FA95500810161~~ FA9550-05-1-0206

Aluminum particles are often ingredients in modern solid fuel propellants, with some compositions containing as much as 22% aluminum in the form of 50 -100  $\mu\text{m}$  diameter aluminum particles. Not surprisingly, combustion reactions between these particles and their co-fuel(s) are significantly influenced by particle surface areas and other interfacial effects. Burning rates could presumably be improved by using smaller aluminum particles, but efforts in this direction have been impeded by the strong tendency of ultra-small aluminum particles to oxidize. Below diameters of  $\sim 30$  nm, for example, nominally pure aluminum particles are typically found to have oxidized to mostly aluminum oxide, i.e., only a small core of unreacted aluminum metal survives within an alumina "overcoat". Aluminum nanoparticles are incredibly reactive! An ideal aluminum-containing solid fuel would be composed of extremely small, unoxidized aluminum clusters, evenly dispersed amongst its co-fuel molecules, so that the combustion reaction could proceed almost homogeneously rather than heterogeneously. Also, an ideal fuel would have to release substantial amounts of energy and copious quantities of gaseous combustion products.

Our efforts toward identifying such materials have focused on four distinct approaches. In one, we concentrated on studying covalent aluminum-containing molecular/cluster units, especially novel aluminum hydride clusters/molecules. In another, we investigated the reactivity of aluminum cluster anions. In the third, we and our collaborators explored synthesizing derivatives of aluminum hydride clusters/molecules. And in the fourth, we have explored the prospects of making prototypical salt "molecules", composed of cations and aluminum-containing cluster anions. After describing how we conducted our experiments, we will first

summarize our work with aluminum hydride systems, then describe our work studying aluminum cluster anion reactivity and synthesis, and lastly summarize our studies with ionic aluminum cluster-containing salts.

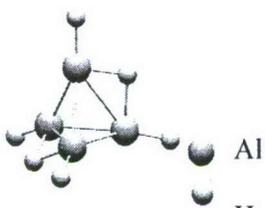
Our primary experimental protocol involved utilizing specialized cluster anion sources for generating the species of interest, mass spectrometry for identifying and mass-selecting them, and anion photoelectron spectroscopy for determining electronic information about a given cluster anion's corresponding *neutral*. Negative ion photoelectron (photodetachment) spectroscopy is conducted by crossing a mass-selected, cluster anion beam with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. Photodetachment of an electron from an anion accesses the vibronic states of its neutral counterpart at the structure of that anion. Within this condition, the photoelectron spectrum of an anion thus provides the electronic state splittings of its corresponding neutral along with the electron affinity value. In our apparatus, photodetachment is accomplished with a Nd:YAG laser, and electron energy analysis is provided by a magnetic bottle electron energy analyzer.<sup>18</sup> Two main types of sources are used, laser vaporization sources (several variants) and a pulsed arc discharge source (PACIS). In one case, a laser pulse impinges on a target, while in the other case, an electric discharge impinges on a target. In both cases, a pulsed jet of helium is coordinated with the vaporizing pulse. Mass analysis and selection is accomplished with a time-of-flight mass spectrometer.

### **Aluminum Hydride Clusters/Molecules**

During the previous grant cycle, we investigated a wide variety of aluminum hydride clusters/molecules, discovering a whole new family of previously unknown aluminum hydride

molecules/clusters. Whereas boron has many hydrides, aluminum had been thought to exhibit only a few. We were able to make and characterize over a hundred, previously unknown aluminum hydride species. Moreover, a considerable number of them exhibit significant stability as reflected in both their measured and calculated HOMO-LUMO gaps. Thus, some of these hydrides may well be candidates as fuels for propulsion applications. Below, we summarize several of our studies with these systems.

**Al<sub>4</sub>H<sub>6</sub>** A combined anion photoelectron and density functional theory computational study of the Al<sub>4</sub>H<sub>6</sub><sup>-</sup> anion, and its corresponding neutral, Al<sub>4</sub>H<sub>6</sub>, showed that Al<sub>4</sub>H<sub>6</sub> can be

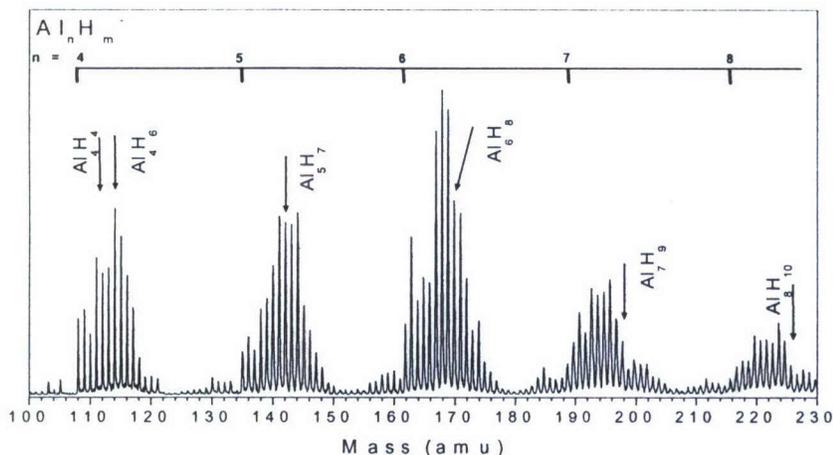


understood in terms of the Wade-Mingos rules for electron counting, suggesting that it may be a borane analog. The data support an Al<sub>4</sub>H<sub>6</sub>

Al structure with a distorted tetrahedral aluminum atom framework, four terminal Al-H bonds, and two sets of counter-positioned Al-H-Al

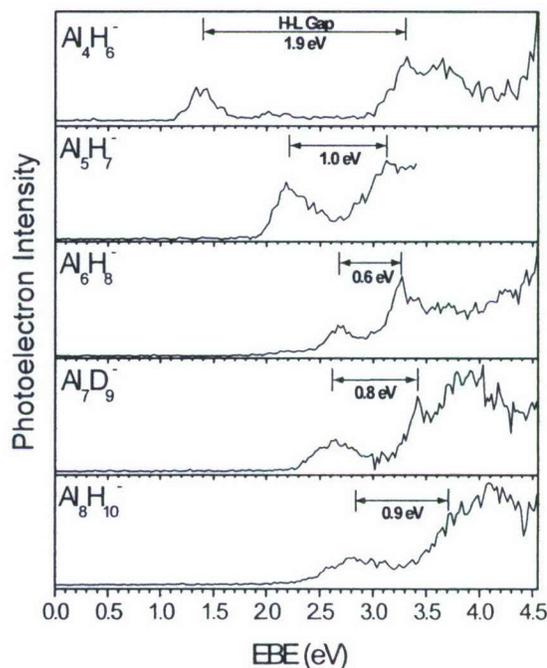
bridging bonds. The large HOMO-LUMO gap found for Al<sub>4</sub>H<sub>6</sub> together with its exceptionally high heat of combustion further suggests that Al<sub>4</sub>H<sub>6</sub> may be an important energetic material, if it can be prepared in bulk. Unlike boranes, the reaction of these aluminum hydrides with oxygen would be likely to go to completion, leading to Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O and thus to a high energy release. Our paper describing these results was published in *Science* **315**, 356 (2007).

**Closo-Alanes (Al<sub>4</sub>H<sub>4</sub>, Al<sub>n</sub>H<sub>n+2</sub>, 4 ≤ n ≤ 8)** Anion photoelectron spectroscopy and density functional theory were also employed to study the wider aluminum hydride cluster family, Al<sub>n</sub>H<sub>m</sub><sup>-</sup> (4 ≤ n ≤ 8, 0 ≤ m ≤ 10). Photoelectron spectra revealed that Al<sub>4</sub>H<sub>4</sub>, Al<sub>4</sub>H<sub>6</sub> and a family of species with general formula Al<sub>n</sub>H<sub>n+2</sub> (5 ≤ n ≤ 8) have small adiabatic electron affinities and large HOMO-LUMO gaps (ranging from 0.5 to 1.9 eV) relative to those of their stoichiometric neighbors, implying their enhanced stabilities. Formulas reminiscent of boranes



led us to investigate whether Wade's rules could be applied to alanes as well. DFT calculations showed that the  $\text{Al}_n\text{H}_{n+2}$  ( $5 \leq n \leq 8$ ) family adopts  $n$ -vertex polyhedral closo-structures with two extra

hydrogen atoms occupying opposite bridging positions in agreement with the Wade's ( $n + 1$ ) rule. These can be viewed as aluminum versions of hypothetical diprotonated closo-borane dianions ( $\text{B}_n\text{H}_n^{2-} + 2\text{H}^+$ ). In addition,  $\text{Al}_4\text{H}_4$  assumes a closo-tetrahedral geometry, and  $\text{Al}_4\text{H}_6$ , as discussed above, takes on a distorted tetrahedral ( $D_{2d}$ ) structure. All of these species can be understood in terms of underlying Polyhedral Skeletal Electron Pair Theory (PSEPT) concepts. Although, the herein studied alanes do not have direct borane analogs, the ability to understand their structures in terms of the Wade-Mingos rules and the underlying PSEPT concepts suggests that they can be considered as borane analogs, thereby opening a new chapter in aluminum hydride chemistry. Our paper describing these results was published in *J. Am. Chem. Soc.* **129**, 5969 (2007).



**$\text{Al}_3\text{H}^-$ : Hydrogen Atom Site-Selectivity and the Shell Model** We also explored the influence of the shell model on H-atom site-selectivity in  $\text{Al}_3\text{H}^-$ . Photoelectron spectra revealed

that  $\text{Al}_{13}\text{H}^-$  has two isomers and for both of them provided vertical detachment energies (VDE) for their anions and adiabatic electron affinities ( $\text{EA}_a$ ) for their corresponding neutrals. Theoretical calculations yielded structures of these isomers that differ by the position of the hydrogen atom; in one isomer the hydrogen atom is radially bonded while in the other hydrogen caps a triangular face. The relative energies for both isomers in their anionic and their neutral charge states as well as  $\text{EA}_a$  and VDE values for both isomers were also calculated. Comparison of calculated and measured detachment energies reconciled the spectrum of each isomer with its structure. Shell model, electron counting considerations correctly predicted the relative stabilities of the anionic isomers as well as those of the neutral isomers. Our paper describing these results has been submitted to *J. Chem. Phys.*

**A Generalized Stability Criterion Based on the Shell Model** Using an electronic shell closure criteria, we proposed a new electron counting rule that enables the prediction of the size, composition, and structure of many hitherto unknown, but especially stable clusters consisting of hydrogen and aluminum atoms. The validity of this rule was established through a synergy between anion photoelectron spectra and DFT calculations. Magic clusters, characterized by unusual stability and large HOMO-LUMO gaps, can form the building blocks of cluster-assembled materials, and this rule provides a powerful tool with which to search for them. Our paper describing these results has been published in *Phys. Rev. Lett.* **98**, 256802 (2007).

We also have results in which (1) very high intensities of aluminum cluster anion, magic number species ( $n=13$  and  $23$ ) were produced as a result of post-annealing, (2) anomalous (H vs. D) isotopic effects were observed in the photoelectron spectra of several aluminum cluster anions, and (3) aluminum cluster anions were generated due to the laser-assisted decomposition of alanates. Each of these three studies will be submitted for publication soon.

## $\text{Al}_n^-$ Reactivity Studies

<b>Our <math>\text{Al}_n^-</math> Reactivity Results</b>	
$\text{O}_2$	<ul style="list-style-type: none"><li>• Spontaneous reactions with even sizes, n.</li><li>• Slower, but spontaneous reactions with odd sizes, except n = 13.</li><li>• <math>\text{Al}_{13}^-</math> does not react even over long periods.</li><li>• But, when energy is added (RF pulses), <math>\text{Al}_{13}^-</math> reacts.</li></ul>
HCl	<ul style="list-style-type: none"><li>• Spontaneous reactions with all sizes except n = 13.</li><li>• But, when energy is added (RF pulses), <math>\text{Al}_{13}^-</math> reacts.</li></ul>
$\text{NH}_3$	<ul style="list-style-type: none"><li>• Reacts preferentially with n = 11 and 12.</li><li>• Also reacts with other sizes, but more slowly.</li><li>• With n = 13, its hydride is formed.</li></ul>
$\text{Cl}_2$	<ul style="list-style-type: none"><li>• Reacts spontaneously with all sizes, including n = 13.</li></ul>
$\text{O}_3$	<ul style="list-style-type: none"><li>• Reacts spontaneously with all sizes, including n = 13.</li></ul>

The reactivity of  $\text{Al}_n^-$  cluster anions with various reactants goes to the issue of their stabilities in various chemical environments. We conducted two types of reactivity studies. In one, we generated aluminum cluster anions in a laser or a pulsed arc source and then added a reactant gas downstream in a mini-flow tube, looking for the formation of new species and/or the loss

(etching) of old ones. In the case of ammonia, this resulted in the preferential loss of  $\text{Al}_{11}^-$  and  $\text{Al}_{12}^-$ . In the other type of study, we collaborated with Dr. Schnoekel's group in Karlsruhe, using an FT (ICR) mass spectrometer to study reactions between specific  $\text{Al}_n^-$  cluster anions and various reactants. The advantages of this technique included mass-selectivity and the ability to store specific ions and to follow individual mechanistic steps. Combined with calculations to help us follow the energetics, this produced a comprehensive picture of the mechanisms for these reactions. To facilitate this collaboration, one of my students made two extended trips there, I made two, and one of Dr. Schnoekel's students made one extended visit here. Together, we studied the reactions of  $\text{Al}_n^-$  with five reactants, and highlights of these studies are shown in the accompanying table. Several papers have been published, one in *Angew. Chem. Int. Ed.* **45**, 1

(2006), another in *J. Am. Chem. Soc.* **128** 7904 (2006) and still another in *Science* **319**, 438 (2008) in which we showed that their reactivity is controlled by spin conservation rules.

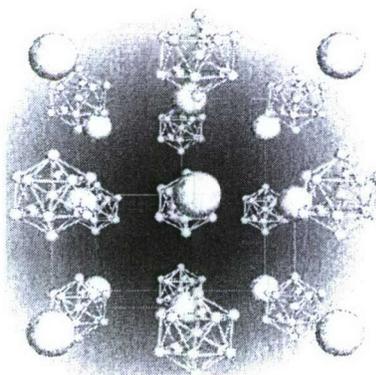
### **Bulk Synthesis of Aluminum Hydride Derivatives**

As part of our collaboration, Dr. Schnoeckel's group has synthesized crystals of  $\text{Al}_4(\text{PBU}_2)_6$  and  $\text{Al}_4(\text{PMe}_2)_5\text{Br}$ , the first structurally-characterized analogs (derivatives) of  $\text{Al}_4\text{H}_6$ . The preparation of these compounds in macroscopic quantities is a milestone in our efforts to make the leap from isolated molecules to real materials, i.e., "from beams to beakers".



### **Ionic "Molecules" in which their Negatively-Charged Moieties are Aluminum-Containing Cluster Anions**

The cluster anion  $\text{Al}_{13}^-$  is unusually stable for two reasons: it is a 40 valence electron shell model, closed shell species, and it has an icosahedral geometry with one aluminum atom inside the cage. It also has the same electron detachment energy (negative of the electron affinity) as does  $\text{Cl}^-$ . For that reason, it has been proposed that  $\text{Al}_{13}^-$  might replace  $\text{Cl}^-$  in ionic molecules,



making salt-like "molecules" such as  $\text{KAl}_{13}$ , which are actually the species,  $\text{K}^+\text{Al}_{13}^-$ . These species were then envisioned as possible building blocks for extended ionic lattices in macroscopic materials as visualized at left. We have made a variety of these species in beams and taken their photoelectron spectra.

## Publications Resulting from this Work:

1. R. Burgert, H. Schnöckel, M. Olzmann, and K. H. Bowen, "The Chlorination of the  $[Al_{13}]^-$  Cluster and the Stepwise Formation of Its Intermediate Products,  $[Al_{11}]^-$ ,  $[Al_9]^-$ , and  $[Al_7]^-$ : A Model Reaction for the Oxidation of Metals?" *Angew. Chem. Int. Ed.* **45**, 1476-1479 (2006).
2. R. Burgert, S. T. Stokes, K. H. Bowen, and H. Schnöckel, "Primary Reaction Steps of  $Al_{13}^-$  Clusters in an HCl Atmosphere: Snapshots of the Dissolution of a Base Metal", *J. Am. Chem. Soc.* **128**, 7904-7908 (2006).
3. X. Li, A. Grubisic, S. T. Stokes, J. Cordes, G. F. Ganteför, K. H. Bowen, B. Kiran, M. Willis, P. Jena, R. Burgert, and H. Schnöckel, "Unexpected Stability of  $Al_4H_6$ : a Borane Analog?" *Science* **315**, 356-358 (2007).
4. A. Grubisic, X. Li, G. F. Ganteför, K. H. Bowen, B. Kiran, P. Jena, R. Burgert, and H. Schnöckel, "Closo-Alanes ( $Al_4H_4$ ,  $Al_4H_{n+2}$ ,  $4 \leq n \leq 8$ ): A New Chapter in Aluminum Hydride Chemistry", *J. Am. Chem. Soc.* **129**, 5969 (2007).
5. A. Grubisic, X. Li, S. T. Stokes, G. F. Ganteför, K. H. Bowen, B. Kiran, P. Jena, R. Burgert, and H. Schnöckel, " $Al_{13}H^-$ : Hydrogen Atom Site-Selectivity and the Shell Model", *J. Chem. Phys.* (submitted).

6. B. Kiran, P. Jena, X. Li, A. Grubisic, S. T. Stokes, G. F. Ganteför, K. H. Bowen, R. Burgert, and H. Schnöckel, "A Magic Rule for Magic Clusters", *Phys. Rev. Lett.* **98**, 256802 (2007).
7. X. Li, A. Grubisic, G. F. Ganteför, K. H. Bowen, R. Burgert, H. Schnöckel, and A. Martinez, "Selective Etching of  $Al_{11}^-$  and  $Al_{12}^-$  by Ammonia", *J. Chem. Phys.* (in preparation).
8. R. Burgert, H. Schnöckel, S. T. Stokes, and K. H. Bowen, "Primary Steps and Selection Rules for the Attack of  $O_2$  and  $O_3$  on  $Al_{13}^-$  Clusters", *Science* **319** 438 (2008).
9. P. Henke, H. Schnöckel, and K. H. Bowen, "Crystalline  $Al_4(PBu_2)_6$ : The First Structurally Characterized Analog to  $Al_4H_6$ ", *J. Am. Chem. Soc.* (in preparation).