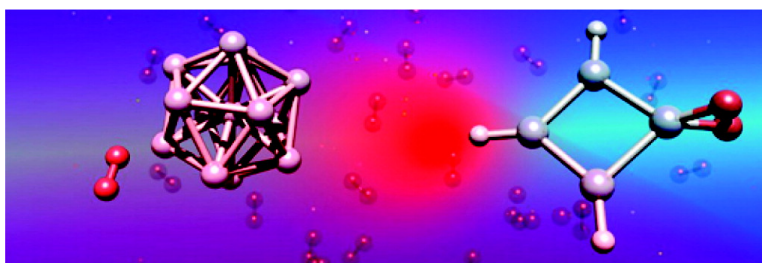Article

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Spin Accommodation and Reactivity of Aluminum Based Clusters with O_2

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Abstract: It is shown that spin accommodation plays a determining role in the reactivity of aluminum based anion clusters with oxygen. Experimental reactivity studies on aluminum and aluminum−hydrogen clusters show variable reactivity in even electron systems and rapid etching in odd electron systems. The reactivity of even electron clusters is governed by a spin transfer to the singlet cluster through filling of the spin down antibonding orbitals on triplet oxygen. Theoretical investigations show that when the spin transfer cannot occur, the species is unreactive. When spin accommodation is possible, more subtle effects appear, such as the required spin excitation energy, which raises the total energy of the system, and the filling of the antibonding levels of the O_2 molecule, which is stabilized by becoming an aluminum oxygen π bond. This explanation is consistent with observed behavior in oxygen etching reactions with a variety of clusters including $Al_nH_m^-$, Al_n^-, $Al_nI_m^-$, and Al_nC^-. The proposed reaction mechanism lends a physical interpretation as to why the HOMO−LUMO gap successfully predicts oxygen etching behavior of the considered systems.

Introduction

The reactivity of metal clusters with molecular oxygen is important for understanding the stability of clusters and the reactivity of catalysts. Oxygen is a strong etchant, and consequently, stable clusters including those with shell closure can be identified via their resistance to etching. Accordingly, etching behavior has been used as an important probe to identify stable species such as superatoms.[1−12] Indeed, numerous studies on the effect of size, shape, and charged state on the reactivity of pure and compound metal clusters have been carried out.[13−17]

These studies indicate that clusters with a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are generally nonreactive.[4,13,14] Second, understanding oxidation is important in catalysis. For example, the study of oxidation reactions helps us identify potential catalysts for conversion of CO to CO_2.[18−24] In this regard, small Au_n^- clusters have been found to be excellent catalysts for CO oxidation.[18−20] Both functions require a fundamental understanding of the microscopic mechanisms and features that govern metal−oxygen reactivity. In particular, why are some metal clusters etched readily, while others are resistant to reaction?

Molecular oxygen is spin triplet in its ground state, and the lowest two unfilled orbitals are a pair of minority orbitals that are antibonding in nature. The most likely reaction product with small aluminum clusters is AlO_2^-, which has a spin singlet ground state, although larger sizes are likely to produce small Al_n^- and neutral oxides.[15] Furthermore, reactivity requires the filling of the minority LUMOs in $^3O_2$. The filling of these

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(1) Khanna, S. N.; Jena, P. *Phys. Rev. Lett.* **1992**, *69*, 1664.

(2) Baruah, T.; Pederson, M. R.; Zope, R. J.; Beltran, M. R. *Chem. Phys. Lett.* **2004**, *387*, 476.

(3) Bergeron, D. E.; Castleman, A. W., Jr.; Morisato, T.; Khanna, S. N. *Science (Washington, DC, U.S.)* **2004**, *304*, 84.

(4) Bergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N. O.; Khanna, S. N. *Science (Washington, DC, U.S.)* **2005**, *307*, 231.

(5) Reveles, J. U.; Khanna, S. N.; Roach, P. J.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18405.

(6) Kawamata, H.; Negishi, Y.; Nakajima, A.; Kaya, K. *Chem. Phys. Lett.* **2001**, *337*, 255.

(7) Koyasu, K.; Atobe, J.; Akutsu, M.; Mitsui, M.; Nakajima, A. *J. Phys. Chem. A* **2007**, *111*, 42.

(8) Reber, A. C.; Khanna, S. N.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 10189.

(9) Alonso, J. A.; Lopez, M. J.; Molina, L. M.; Duque, F.; Mananes, A. *Nanotechnology* **2002**, *13*, 253.

(10) Janssens, E.; Neukerman, S.; Lievens, P. *Solid State. Mater. Sci.* **2004**, *8*, 185.

(11) Schnepf, A.; Schnockel, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3532.

(12) Castleman, A. W., Jr.; Khanna, S. N.; Sen, A.; Reber, A. C.; Qian, M.; Davis, K. M.; Peppernick, S. J.; Ugrinov, A.; Merritt, M. D. *Nano Lett.* **2007**, *7*, 2734.

(13) Leskiw, B. D.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **2000**, *316*, 31.

(14) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. *J. Chem. Phys.* **1989**, *91*, 2753.

(15) Cooper, B. T.; Parent, D.; Buckner, S. W. *Chem. Phys. Lett.* **1998**, *284*, 401.

(16) Hettich, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 8582.

(17) Jarrold, M. F.; Bower, J. E. *J. Chem. Phys.* **1987**, *87*, 5728.

(18) Heiz, U.; Sanchez, A.; Abbet, S.; Schneider, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3214.

(19) Zhang, C.; Yoon, B.; Landman, U. *J. Am. Chem. Soc.* **2007**, *129*, 2228.

(20) Reilly, N. M.; Reveles, J. U.; Johnson, G. E.; Khanna, S. N.; Castleman, A. W., Jr. *J. Phys. Chem A* **2007**, *111*, 4158.

(21) Salisbury, B. E.; Wallace, W. T.; Whetten, R. L. *Chem. Phys.* **2000**, 131.

(22) Wallace, W. T.; Wyrwas, R. B.; Whetten, R. L.; Mitric, R.; Bonacic-Koutecky, V. *J. Am. Chem. Soc.* **2003**, *125*, 8408.

(23) Lee, S.; Fan, C.; Wu, T.; Anderson, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 5682.

(24) Hagen, J.; Socaciu, L. D.; Elijazyfer, M.; Heiz, U.; Thorsten, T. M.; Wöste, L. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1707.

orbitals may be thought of as a spin multiplicity $3 \rightarrow 1$ excitation of the oxygen half of the complex and could be facilitated by spin−orbit coupling. However, aluminum and oxygen have negligible spin−orbit effects such that reactions should follow the Wigner−Witmer rules of spin conservation.[25,26] Therefore, the reaction has to conserve the overall spin of the system. For clusters with an odd number of electrons, the spin of the extra electron could align opposite to the majority spin electrons of the $^3O_2$ molecule, and the spin conservation does not require any spin excitation of the metal counterpart. The situation is different for clusters with an even number of electrons since the decrease in the spin multiplicity of the oxygen half of the reacting cluster has to follow the spin excitation of the remaining portion to conserve the total spin. Consequently, the ability of the cluster to become spin excited to accommodate the triplet spin of oxygen must play a role in reactivity.

Experimental and Theoretical Methods

Recently, we have studied the addition of hydrogen atoms to aluminum clusters to generate $Al_nH_m^-$ $(1 \leq n \leq 7)$[27] in an attempt to understand the formation mechanisms of the alane clusters[28,29] and to investigate the evolution of electronic structure one electron at a time. Aluminum-hydride clusters were formed in a fast-flow reactor,[30,31] employing a laser induced plasma technique with a mixed hydrogen/helium carrier gas. The plasma created in the source frees hydrogen atoms, aluminum atoms, and electrons to combine with the aluminum vapor and form mixed clusters. Formation processes are arrested as the gas escapes the source waiting room, entering expansively into a lower pressure laminar flow-tube. Carrier gas is leaked into the source at 8000 sccm, while a ∼0.3 Torr pressure is maintained in the flow-tube by a high-volume roots blower. The clusters are cooled to room temperature through the transfer of excess thermal energy to the chamber walls in collisions with a carrier gas within the laminar flow region. We focus on our results in the $Al_4H_n^-$ series to illustrate the new finding. The original series contained all sizes with higher relative abundances at Al_4^- and $Al_4H_7^-$. The clusters were treated with oxygen to eliminate the reactive species. The mass spectra of the unreacted (Figure 1A) and reacted (Figure 1B) species showed that all the clusters containing even numbers of hydrogen atoms were etched away, while those containing odd numbers of hydrogen atoms survived. Further, while the intensity of $Al_4H_3^-$ and $Al_4H_5^-$ decreases very slightly, that of Al_4H^- and $Al_4H_7^-$ grows with the addition of oxygen.

To probe the mechanism for oxidation and the origin of reactivity in these species, we carried out theoretical investigations on minimum energy configurations obtained by approaching an O_2 molecule with four representative clusters: Al_{13}^-, Al_5^-, $Al_4H_3^-$, and Al_3^-. A first principles molecular orbital approach was used, wherein the cluster wave function is expressed as a linear combination of atomic orbitals centered at the atomic sites. The calculations were performed within a density functional framework using the NRLMOL set of codes[32−34]
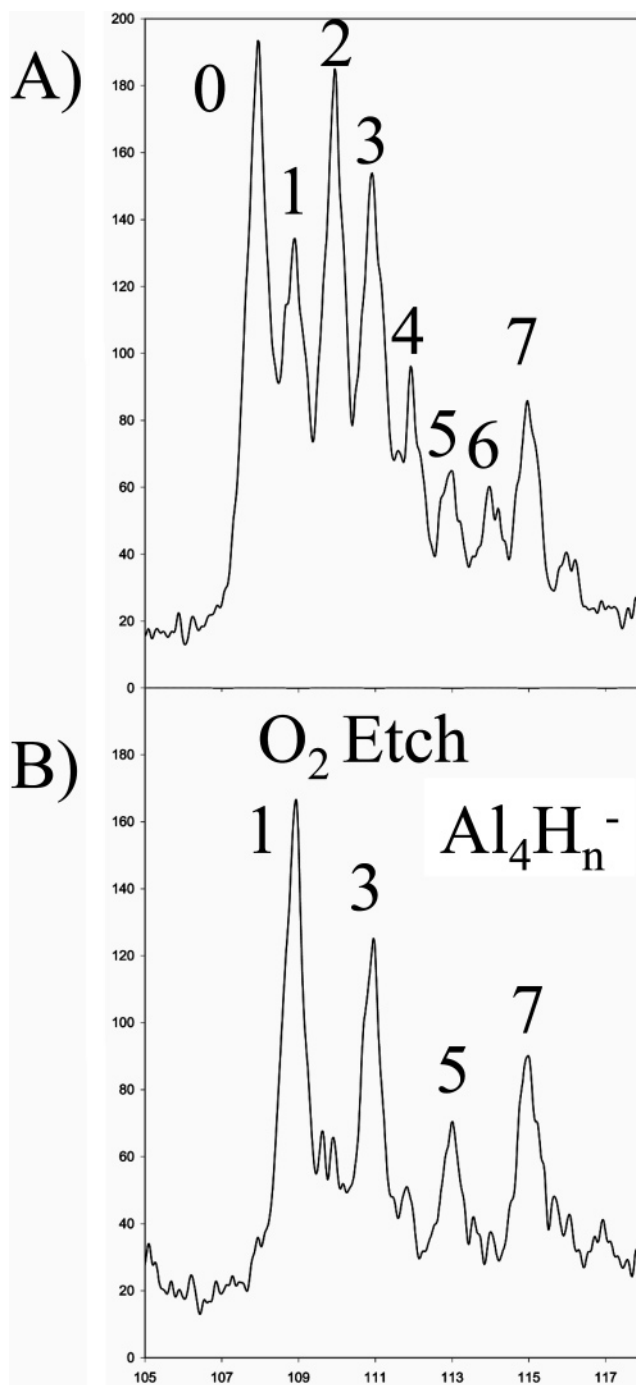

Figure 1. (A) Mass spectrum of $Al_4H_n^-$. (B) Mass spectrum of $Al_4H_n^-$ after exposure to oxygen.

developed by Pederson and co-workers. Here, the wave function of the cluster is expressed as a linear combination of Gaussian orbitals centered at the atomic sites in the cluster. The basis set consisted of 6s, 5p, and 3d functions for Al; 4s, 3p, and 1d Gaussian functions for H; and 5s, 4p, and 3d for O, and the basis sets were supplemented with additional Gaussians. The generalized gradient functional proposed by Perdew et al.[35] was used to incorporate exchange-correlation effects.

Results and Discussion

As an initial test to determine if the spin was playing a role in the select etching of aluminum hydrides, we calculated and

(25) Wigner, E.; Witmer, E. E. *Z. Phys.* **1928**, *51*, 859.
(26) Schwarz, H. *Int. J. Mass Spectrom.* **2004**, *237*, 75.
(27) Roach, P. J.; Reber, A. C.; Woodward, W. H.; Khanna, S. N.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 14565.
(28) Li, X.; Grubisic, A.; Stokes, S. T.; Cordes, J.; Gantefor, F. G.; Bowen, K. H.; Kiran, B.; Willis, M.; Jena, P.; Burgert, R.; Schnokel, H. *Science (Washington, DC, U.S.)* **2006**, *315*, 356.
(29) Grubisic, A.; Li, X.; Stokes, S. T.; Cordes, J.; Gantefor, G. F.; Bowen, K. H.; Kiran, B.; Jena, P.; Burgert, R.; Schnockel, H. *J. Am. Chem. Soc.* **2007**, *129*, 5969.
(30) Guo, B. C.; Wei, S.; Chen, Z.; Kerns, K. P.; Purnell, J.; Buzza, S.; Castleman, A. W., Jr. *J. Chem. Phys.* **1992**, *97*, 5243.
(31) Castleman, A. W., Jr.; Weil, K. G.; Sigsworth, S. W.; Leuchtner, R. E.; Keesee, R. G. *J. Chem. Phys.* **1987**, *86*, 3829.
(32) Pederson, M. R.; Jackson, K. A. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, 7453.
(33) Jackson, K.; Pederson, M. R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *42*, 3276.
(34) Porezag, D.; Pederson, M. R. *Phys. Rev. A: At., Mol., Opt. Phys.* **1999**, *60*, 2840.
(35) Perdew, J. P.; Burke, K.; Enzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

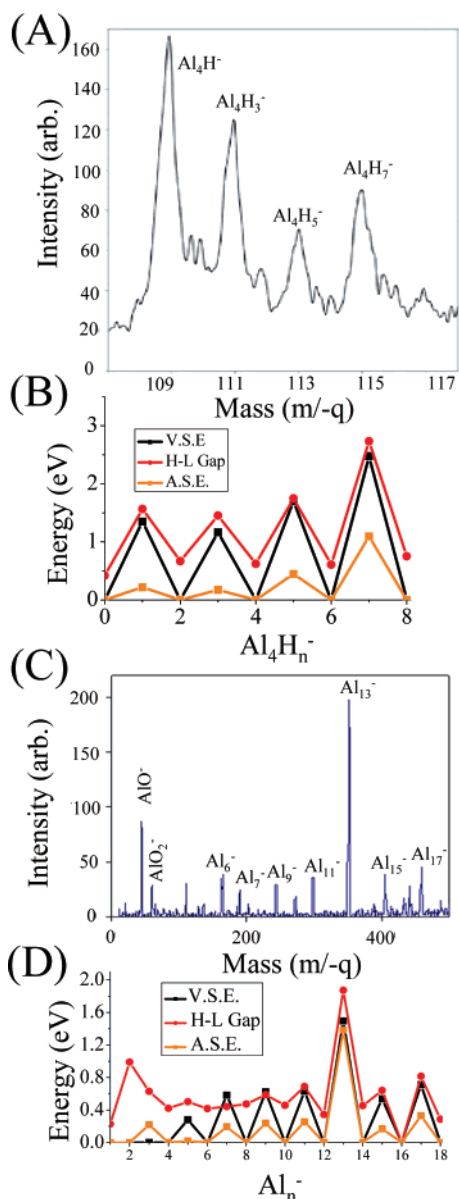## (A)

(B)

(C)

(D)

Figure 2. (A) Mass spectrum of $Al_4H_x^-$ clusters after exposure to oxygen. (B) HOMO−LUMO gap, vertical spin excitation energy, and adiabatic spin excitation energy of $Al_4H_n^-$. (C) Mass spectrum of Al_n^- clusters after exposure to molecular oxygen. (D) HOMO−LUMO gap and vertical and adiabatic spin excitation energies in Al_n^-.

compared three quantities: (1) the energy difference between the HOMO and the LUMO called the HOMO−LUMO gap; (2) the vertical spin excitation, which is the lowest energy required to excite the cluster from a singlet to triplet state, with no geometry rearrangement; and (3) the adiabatic spin excitation energy, which is the difference between the ground state of the triplet and the ground state of the singlet spin spaces. The results are shown in Figure 2B, while Figure 2A shows the mass intensity of the reacted species. Note the strong even−odd effect in both the mass spectrum and the theoretical plot. The odd electron species are treated as having no spin excitation because the combined cluster with O_2 has the same spin multiplicity as the cluster, and no spin excitation is needed. In Figure 2C, we show the mass spectrum of pure aluminum clusters after being exposed to oxygen; Figure 2D shows the calculated spin excitations and HOMO−LUMO gaps in these clusters. Again,
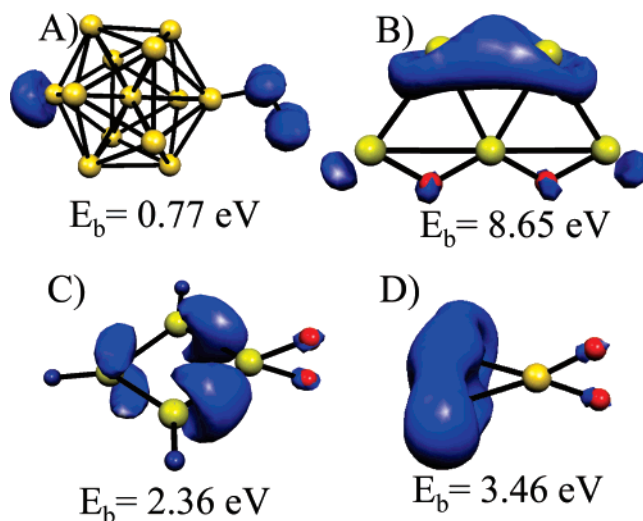

Figure 3. (A) Spin density (blue) plot of $Al_{13}O_2^-$ cluster. E_b indicates binding energy. (B) Spin density plot of $Al_5O_2^-$ complex. (C) Spin density (blue) plot of $Al_4H_3^-$ interacting with O_2 after relaxation. (D) Spin density (blue) plot of $Al_3O_2^-$ complex.

there is a strong correlation between the calculated spin excitation energies and the reactivity.

Figure 2A,C shows that the odd electron species are etched almost completely in both aluminum hydride and pure aluminum distribution. In pure aluminum, Al_{13}^- and Al_{23}^- remain intact, with no observable reactivity.[14,15] Again, note that the calculated HOMO−LUMO gap and spin excitation line up with the etching spectrum nearly exactly. These experimental results lead to three critical questions: (1) why do all odd electron species etch rapidly, (2) why do low-spin excitation energy species etch, and (3) why are high-spin excitation energy species unreactive when exposed to oxidation?

To examine if the observed differences in behavior in these four species are rooted in the spin excitation energy, theoretical investigations were undertaken where an O_2 molecule approached Al_{13}^- from a distance. Figure 3A shows the optimized geometry and spin density of the resulting complex, obtained by taking the difference between the spin up and the spin down charge density. Also given is the net binding energy of the O_2 molecule to the cluster calculated using the equation

$$BE = E(^3O_2) + E(^1Al_{13}^-) - E(^3Al_{13}O_2^-) \quad (1)$$

The energy required to excite an O_2 molecule from triplet to singlet is 0.98 eV. Our calculations show that Al_{13}^- has a large adiabatic spin excitation energy of 1.38 eV, and one finds (Figure 3A) that the spin is not transferred to the aluminum cluster (it is essentially located on the oxygen molecule). In Figure 4A, we plot the one electron levels and see that the antibonding orbitals (blue) in the cluster are unfilled, confirming the cluster's electronic stability and resistance to spin accommodation. To further confirm this hypothesis, we used theory to investigate the reaction between Al_{13}^- and singlet O_2. If the cluster was protected merely by its large electron affinity, 3.40 eV (and the HOMO−LUMO gap), it would also be inert against singlet oxygen. By contrast, we found the O−O bond to break and the O atoms inserted into the cluster. The large spin excitation energy also accounts for the previously observed resistance of $Al_{13}I_{2n}^-$, $Al_{14}I_{2n+1}^-$, and Al_7C^- clusters to reactivity

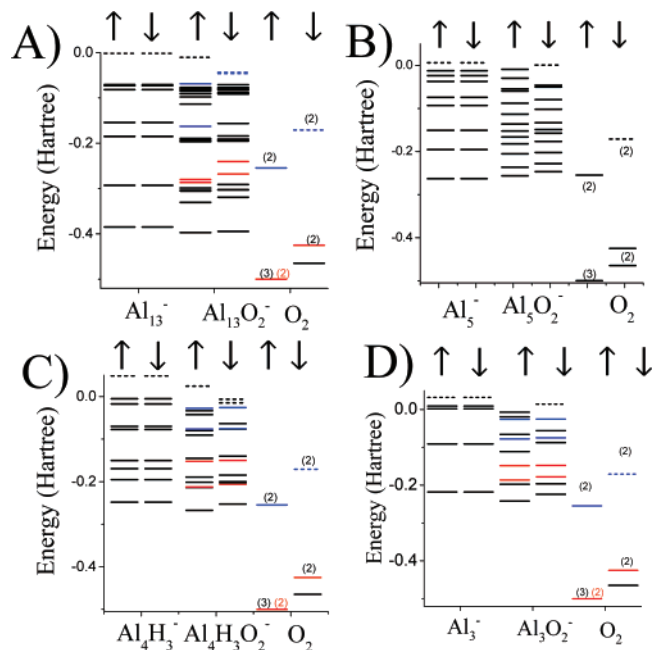**Figure 4.** One electron levels for (A) $Al_{13}O_2^-$, (B) $Al_5O_2^-$, (C) $Al_4H_3O_2^-$, and (D) $Al_3O_2^-$ complex, along with levels for the pure cluster and oxygen. Blue indicates π^* levels, and red indicates π levels.

with oxygen. The $Al_{13}I_{2n}^-$ and $Al_{14}I_{2n+1}^-$ clusters have the same HOMO−LUMO gap as Al_{13}^- and show similar spin excitation energies.[8] For Al_7C^-, our calculations indicate a very large adiabatic excitation energy of 1.13 eV.[3−5,13]

Next, we consider $^1Al_5^-$, which is completely etched in the experimental spectrum yet has an even number of electrons. The adiabatic spin excitation energy is only 0.01 eV, so it is expected that the spin will be readily transferred to the cluster. To examine it, an O_2 molecule was brought toward the cluster, and the geometry was optimized by moving atoms in the direction of forces. Once the optimization was complete, the oxygen had completely inserted into the aluminum cluster, and no oxygen−oxygen bond remained (Figure 2B). This is the same result that is seen in odd electron structures, where the spin excitation energy can be thought of as effectively zero since no spin excitation is needed.[21] The spin transfer populates both antibonding orbitals, and the activated oxygen reacts readily with minimal energetic cost to the rearrangement of the cluster.

Now that we have observed two extreme cases where the excitation energy is singularly large and essentially zero, what about more subtle effects on the reactivity? To examine this, we placed O_2 at some distance from an $Al_4H_3^-$ cluster, which has a very respectable vertical spin excitation energy of 1.16 eV but an adiabatic energy of only 0.17 eV. In Figure 3C, we see that the O−O bond remains intact but has stretched to 1.58 Å and that the binding energy is 2.36 eV. A Mulliken population analysis showed a net charge of −1.0 on the O_2 molecule. Our finding showed that the O−O bond only broke if the molecule was brought very close to the cluster. Through studies of the energy of the combined system as a function of O−O distance, we found a barrier of around 0.4 eV for the breaking of the O−O bond. What is striking here is that the spin has transferred fully to the cluster. If we look at the electronic structure in Figure 4C, the antibonding orbitals are filled, and the bond order of the O−O bond is one. The presence of the barrier shows that the electronic rearrangement has a cost, which decreases the reactivity of the cluster despite the population of the antibonding

orbitals and essentially completes spin transfer. The spin excitation energy between the ground state of $^1Al_4H_3^-$ and the ground state of $^3Al_4H_3^-$ in the geometry observed here is 0.82 eV. However, the species apparently does not assume the triplet ground state. To more clearly demonstrate the role of excitation energy, we look at a comparable local minimum in a cluster that is readily etched, namely, Al_3^-.

If Figure 3D, we show the geometry and spin density of the $Al_3^-−O_2$ complex. Several initial approaches resulted in complete breaking of the O−O bond; however, we are interested in comparing the difference in the binding energy and electronic levels in a case with modest and negligible spin excitation energies. First of all, the binding energy of O_2 has increased 1.1 eV from the Al_5^- complex to 3.46 eV. Further, the Mulliken charge on O_2 was the same as in $Al_4H_3^-$. The enhancement in binding could be rationalized on the basis that the spin excitation energy of the cluster is small as compared to the 0.82 eV spin excitation energy needed to bind an O_2 in the case of $Al_4H_3^-$. To further examine the origin of the stability, we compared the electronic levels of the $Al_4H_3^-$ complex with Al_3^- in Figure 4D. In $Al_4H_3^-$, the antibonding states make up both HOMOs, while in Al_3^-, the state is buried deeper within the electronic structure. This suggests that the Al−O interaction is strengthened by the low-cost spin accommodation, as well as by the π bond of the Al−O orbitals. Therefore, the spin excitation energy does not only spin protect closed shell species such as Al_{13}^- that have large spin excitation energies, but it can also reduce the interaction between Al and O_2 in cases where the spin accommodation is possible. This can lead to the observed imperfect protection and consequently a slower etching.

Conclusion

In conclusion, we have shown that the spin excitation energy controls the reactivity of aluminum based anion clusters in both vivid and subtle ways. Magic clusters such as Al_{13}^-, which have a high-spin excitation energy, are highly resistant to etching and are not observably reactive, while odd electron and low excitation energy species react readily. In intermediate cases, if the spin transfer occurs the binding energy of molecular oxygen is less than cases in which the spin excitation energy is small. This analysis provides a physical interpretation as to why clusters with high HOMO−LUMO gaps are resistant to oxygen etching, as such species generally have large spin excitation energies unless significant rearrangements occur. It also confirms that oxygen etching experiments are a useful method for filtering molecular beams with a diversity of potential species for those that have a special electronic stability. This also brings out the interesting possibility of tuning electronic structures to design more efficient catalysts. This can be accomplished (e.g., by doping clusters with selected transition metal atoms to reduce the spin transition energy or changing the multiplicity of the reactant). On the other hand, the clusters can be made more resistant to corrosion by increasing the excitation energy through closing electronic shells and assuring that they have a large spin excitation.

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