

# 論文の内容の要旨

論文題目 Structure and stability of aluminum clusters containing icosahedral units  
(正二十面体ユニットを含むアルミニウムクラスターの構造と安定性)

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## 1. Introduction

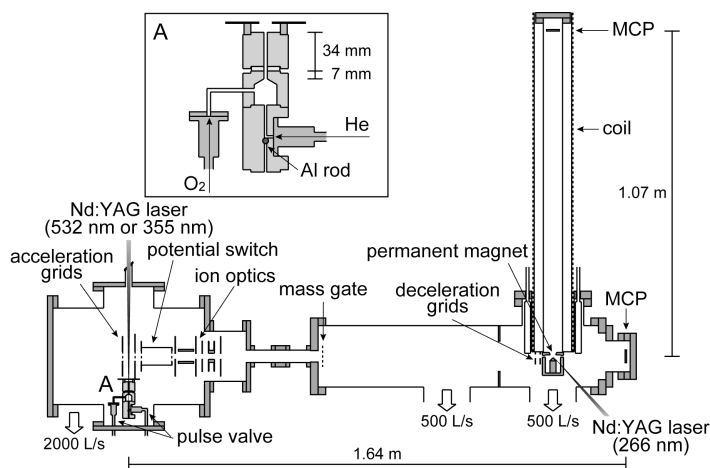
Clusters of simple metals such as Na, Au, and Al gain high stability when the superatomic orbitals are completely filled with the valence electrons.<sup>1</sup>  $\text{Al}_{13}^-$ , one of the most extensively studied magic clusters, has a closed electronic configuration with 40 valence electrons and a highly symmetrical icosahedral motif. Thus,  $\text{Al}_{13}^-$  has attracted much attention as a building unit of cluster-based nanomaterials. Although several  $\text{Al}_{13}$ -containing complexes such as  $\text{Al}_{13}\text{Na}$  and  $\text{Al}_{13}\text{I}^-$  have been successfully formed in gas phase,<sup>2,3</sup> chemical synthesis of  $\text{Al}_{13}$ -based materials has been a challenge in cluster science. In addition,  $\text{Al}_{13}^-$  is known to be robust against oxidation by  $\text{O}_2$ , whereas other  $\text{Al}_n^-$  are easily etched into smaller clusters by consecutively release of  $\text{Al}_2\text{O}$  fragments.<sup>4,5</sup>

The aim of the thesis is to provide a clue for the synthesis of  $\text{Al}_{13}$ -based materials by a combined approach of experimental and theoretical calculation. In chapter 2, I studied reactions of  $\text{Al}_n^-$  under high-pressure  $\text{O}_2$  to gain insights into the stability of  $\text{Al}_n^-$  under atmospheric conditions. In chapter 3, I computationally investigated the interaction between  $\text{Al}_{13}$  and electron donating ligand to stabilize  $\text{Al}_{13}$  by electronic shell closure.

## 2. Production of new aluminum oxide clusters $\text{Al}_{14}\text{O}^-$ and $\text{Al}_{15}\text{O}_2^-$ having $\text{Al}_{13}$ icosahedral cores

The experiment was conducted as follows using the apparatus shown schematically in Figure 1. First, Al cluster anions were produced by focusing the second or third harmonics of an Nd:YAG laser onto a

rotating Al target rod (99.99%) under a high-pressure helium gas (99.995%) supplied by a pulsed valve. Then, the  $\text{Al}_n^-$  clusters were allowed to react with  $\text{O}_2$  (99.5%) introduced by another pulsed valve. Finally, the reaction products were extracted into a time-of-flight mass spectrometer by applying a pulsed electric field. The photoelectron spectra of the mass-selected products were recorded by irradiating the fourth harmonic of an

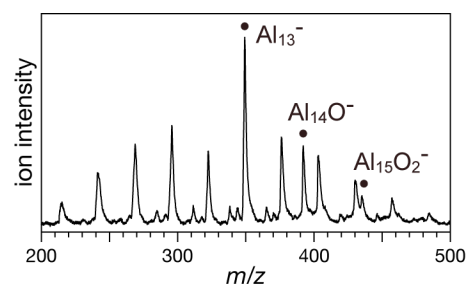


**Figure 1.** Schematic of the experimental apparatus.

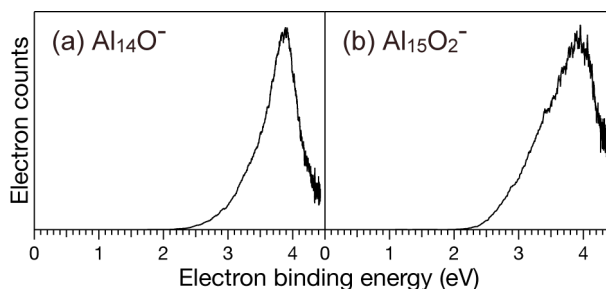
Nd:YAG laser. The photoelectrons were collected by a strong magnetic field ( $\sim 1000$  G) produced by a permanent magnet and guided by a weak magnetic field ( $\sim 10$  G) produced by a solenoid coil to a time-of-flight electron spectrometer. Electronic and geometrical structures of Al clusters were calculated by density functional theory (DFT) at the level of B3LYP/6-31G(d) using the Gaussian 09 package. The vertical detachment energy (VDE) was calculated as the energy difference between the ground state of the anion and that of the neutral cluster with the geometry of the anion.

Figure 2 show a typical mass spectrum of Al cluster anions after reaction with  $\text{O}_2$ . As reported previously,<sup>4,5</sup>  $\text{Al}_{13}^-$  showed high tolerance against  $\text{O}_2$  whereas the intensities of other sized  $\text{Al}_n^-$  clusters were reduced significantly because of consecutive etching reactions by  $\text{O}_2$ . Interestingly, two new aluminum oxide clusters,  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$  were observed for the first time in the reaction of  $\text{Al}_n^-$  and  $\text{O}_2$ . The VDEs of  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$  were determined to be  $3.84 \pm 0.02$  and  $3.88 \pm 0.02$  eV, respectively, from the photoelectron spectra (Figure 3). The most stable structures of  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$  among several isomers can be viewed as icosahedral  $\text{Al}_{13}$  cores and one or two OAl ligand(s), respectively (Figure 4). The VDE values of these structures were calculated to be 3.27 and 3.28 eV, respectively, and reproduced the experimental values.

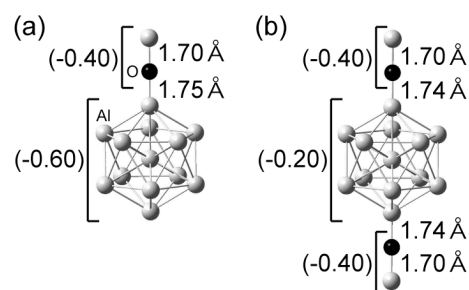
Given that the reaction of  $\text{Al}_n^-$  ( $n \geq 8$ ) with  $\text{O}_2$  proceeds by releasing highly stable fragments  $\text{Al}_2\text{O}$ ,<sup>4,5</sup> the  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$  clusters correspond to intermediates of oxidative etching reactions of  $\text{Al}_{16}^-$  and  $\text{Al}_{15}^-$ ,



**Figure 2.** Mass spectra of  $\text{Al}_n^-$  after reaction with  $\text{O}_2$ .



**Figure 3.** Photoelectron spectra of (a)  $\text{Al}_{14}\text{O}^-$  and (b)  $\text{Al}_{15}\text{O}_2^-$ .



**Figure 4.** Optimized structure of (a)  $\text{Al}_{14}\text{O}^-$  and (b)  $\text{Al}_{15}\text{O}_2^-$ . The numbers in parentheses indicate Mulliken charges.

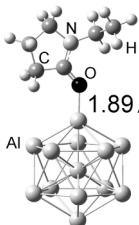
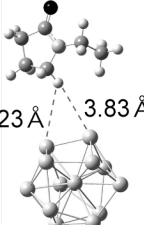
respectively. Thus, the production of unprecedented aluminum oxide clusters in this study is attributable to high activation barrier associated with the release of  $\text{Al}_2\text{O}$  unit(s) from the icosahedral-based structures shown in Figure 4 and efficient collisional cooling by high-pressure of He in the reaction cell. The distribution of the excess charge over the  $\text{Al}_{13}$  core and AlO units (Figure 4) may also contribute to the high stability of  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$ .

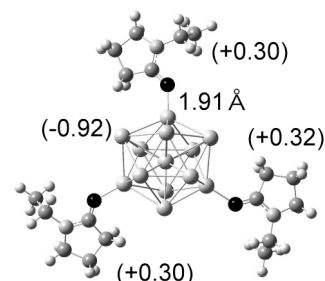
### 3. Stabilization of $\text{Al}_{13}$ icosahedron by electron donating ligand

In order to synthesize  $\text{Al}_{13}$ -based clusters under ambient conditions, we have to overcome several problems: (1) they have to be stabilized against sintering by steric protection; (2) their activity against  $\text{O}_2$  should be reduced by closing the electronic shell by donating one electron.<sup>7</sup> Polyvinylpyrrolidone (PVP) will be suitable to this end since it has been demonstrated that PVP-stabilized Au clusters are negatively charged.<sup>8,9</sup> In order to test the hypothesis, I studied the electronic and geometric structures of complexes between  $\text{Al}_{13}$  and ligand with carbonyl group, especially *N*-ethyl-2-pyrrolidone (EP), which is a monomer unit of PVP. The structures of  $\text{Al}_{13}(\text{EP})_n$  ( $n = 0-4$ ) and  $\text{Al}_{13}^-(\text{EP})_n$  were optimized by DFT at the level of B3LYP/6-31G(d) using Gaussian 09 package. The binding energy (BE) of the EP ligand was estimated by subtracting the total electronic energy of  $\text{Al}_{13}(\text{EP})_n$  from the sum of that of  $\text{Al}_{13}(\text{EP})_{n-1}$  and an EP molecule with the zero-point energy correction. The gross Mulliken charge on the  $\text{Al}_{13}$  moiety in  $\text{Al}_{13}(\text{EP})_n$  ( $\Delta Q$ ) upon the ligation was estimated.

Two structures **1** and **2** were obtained as stable structures of  $\text{Al}_{13}(\text{EP})_1$  (Table 1). In structure **1**, the EP molecule is chemisorbed at the atop site of icosahedral  $\text{Al}_{13}$  via the carbonyl O atom with the BE of 1.11 eV. In structure **2**, the EP is bound weakly (BE = 0.01 eV) with the dipole moment pointing toward  $\text{Al}_{13}$ . The electronic charge of  $\text{Al}_{13}$  moiety is increased by  $-0.36$  e in **1**, whereas no electron transfer occurs in **2**. This indicates that EP can act as an electron donating ligand to  $\text{Al}_{13}$  as in the case of  $\text{Au}_{13}$ .<sup>8</sup> The second and third EP ligands also stabilized  $\text{Al}_{13}$  by electron donation through the carbonyl O atom. The  $\Delta Q$  value was increased monotonically with increasing the number of EP molecules and the  $\Delta Q$  reached almost  $-1$  e in  $\text{Al}_{13}(\text{EP})_3$  (Figure 5). In  $\text{Al}_{13}(\text{EP})_4$ , the fourth EP molecule energetically prefers to be bound to one of the chemisorbed EP ligands via electrostatic interaction rather than to be chemisorbed on  $\text{Al}_{13}$ . The switchover of the bonding scheme of EP at  $\text{Al}_{13}(\text{EP})_4$  suggests that this phenomenon is associated with the closure of electronic shell of the  $\text{Al}_{13}$  moiety in  $\text{Al}_{13}(\text{EP})_3$ . However, spin density analysis revealed that the superatomic orbital 1F of  $\text{Al}_{13}$  remains singly occupied even after chemisorption of three EP ligands. In conclusion, chemisorption of EP ligands to  $\text{Al}_{13}$  does not lead to the filling of the superatomic orbital 1F, but formally

**Table 1.** The optimized structure, BE and  $\Delta Q$  of  $\text{Al}_{13}(\text{EP})_1$ .

	1	2
Optimized structure		
BE (eV)	1.11	0.01
$\Delta Q$ (e)	$-0.36$	$-0.02$



**Figure 5.** Optimized structure of  $\text{Al}_{13}(\text{EP})_3$ .

donates electronic charge through polarized Al–O bonding.

#### 4. Summary

From the reaction of  $\text{Al}_n^-$  and  $\text{O}_2$  under a high-pressure condition, it was confirmed that  $\text{Al}_{13}^-$  is stable even in the high-pressure condition. In addition,  $\text{Al}_{14}\text{O}^-$  and  $\text{Al}_{15}\text{O}_2^-$  were produced for the first time and photoelectron spectroscopy and DFT calculations revealed that these oxide clusters are composed of an icosahedral  $\text{Al}_{13}$  and one or two OAl unit(s), respectively. These ions are intermediates of oxidative etching reaction and their high stability associate with the  $\text{Al}_{13}$  core. On the other hand, from the DFT calculations of structures of  $\text{Al}_{13}(\text{EP})_n$ , it was found that an open-shell  $\text{Al}_{13}$  was stabilized by electron donation from chemisorbed EP ligands via the carbonyl O atom. The total charge accumulated in  $\text{Al}_{13}$  reaches nearly  $-1$  e in  $\text{Al}_{13}(\text{EP})_3$ . The  $\text{Al}_{13}$  moiety stabilized by three EP ligands remains to be an open-shell superatom although it accepts electronic charge through polarized Al–O bonding.

#### 5. References

- [1] Knight, W. D. *et al. Phys. Rev. Lett.* **1984**, 52, 2141. [2] Nakajima, A. *et al. J. Chem. Phys.* **1991**, 95, 7061. [3] Bergeron, D. E. *et al. Science* **2005**, 307, 231. [4] Leuchtner, R. E. *et al. J. Chem. Phys.* **1991**, 94, 1093. [5] Neumaier, M. *et al. J. Am. Chem. Soc.* **2014**, 136, 3607. [6] Burgert, R. *et al. Science* **2008**, 319, 438. [7] Walter, M. *et al. Proc. Natl. Acad. Sci. U.S.A.* **2008**, 105, 9157. [8] Okumura, M. *et al. Chem. Phys. Lett.* **2008**, 459, 133. [9] Tsunoyama, H. *et al. J. Am. Chem. Soc.* **2009**, 131, 7086.