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# Quantum molecular dynamics simulations of the oxidation of aluminum-cyclopentadienyl clusters

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**Abstract.** We report Car-Parrinello molecular dynamics simulations of the oxidation of aluminum-cyclopentadienyl clusters currently being considered as novel fuels or energetic materials. These clusters contain a small aluminum core surrounded by a single organic ligand layer. The aromatic cyclopentadienyl ligands form a very strong bond with surface Al atoms, giving rise to a stable organometallic cluster which crystallizes into a low-symmetry solid-state material. Our calculations of an isolated cluster in oxygen show minimal reaction between the ligand and oxygen molecules at simulation temperatures of 300 and 1000 K. Rather, in all cases O<sub>2</sub> diffuses through the ligand barrier, splits into atomic oxygen upon contact with the aluminum, and forms an amorphous aluminum oxide core. Loss of aluminum-ligand units, as expected from bond strength calculations, is not observed except following significant oxidation. We present simple metrics to quantitatively compare the steric barrier of the outer ligands that limits the oxidation process.

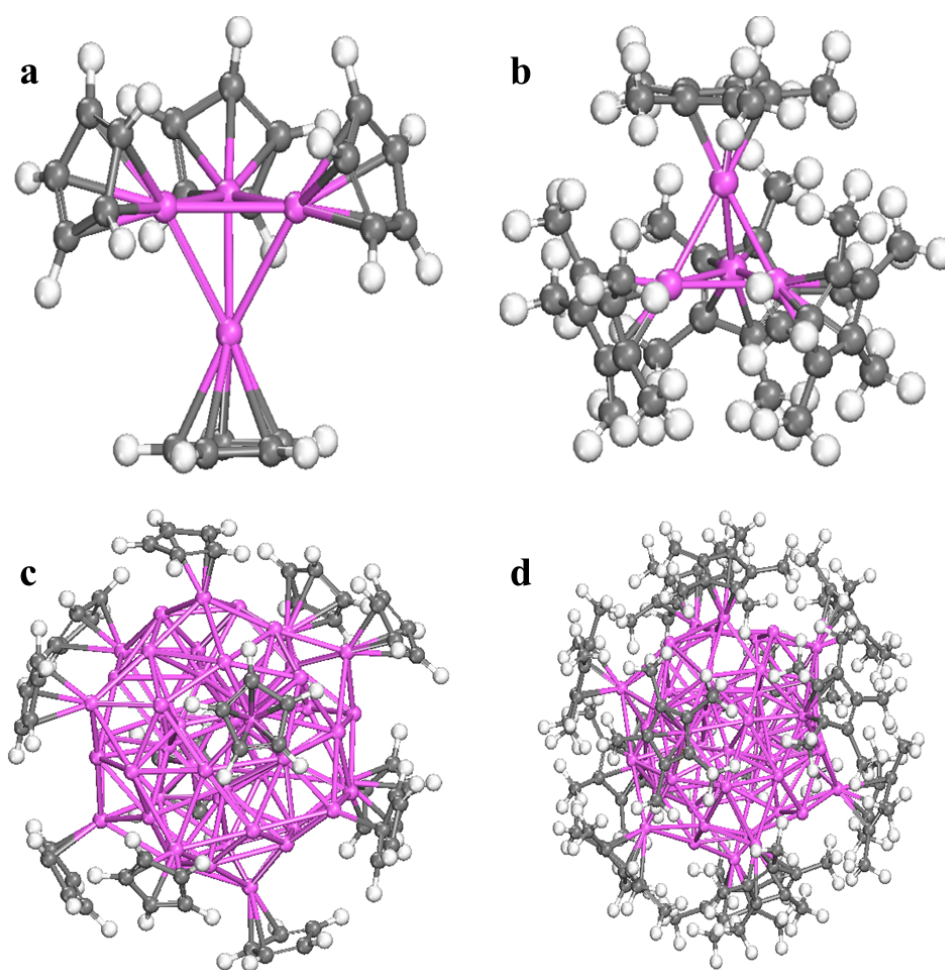
## 1. Introduction

Solid rocket propellants frequently use aluminum powder as a fuel component due to its high enthalpy of combustion. Nanoscale Al fuel has a larger surface to volume ratio, but is limited by its comparatively large surface oxide layer, as well as rapid agglomeration effects of nanoparticle aggregates [1–4]. As a rather different route to rapid aluminium combustion, we have been studying molecular scale aluminium clusters that are passivated against immediate oxidation via a layer of organic ligands. These clusters crystalize into solid-state forms, and in some cases are air stable for sufficient periods of time for basic tests. Bulky ligand groups such as cyclopentadienyl or Cp (C<sub>5</sub>H<sub>5</sub>) and Cp\* (C<sub>5</sub>Me<sub>5</sub>) as well as N(SiMe<sub>3</sub>)<sub>2</sub> have had the most success during the disproportionation synthesis reactions. The reason these particular ligands permit crystallization when many others do not is currently unknown, and computational studies to examine this issue are ongoing. In addition to favoring disproportionation, Cp\* ligands and the like provide a large steric effect which increases the thermal and air stability of the Al core. The air stability provided by these ligands is currently one of the key limiting factors in moving to larger scale testing of these materials, and to date virtually nothing is known about their oxidation (and related to this, their combustion) properties [5].

Our previous density functional theory calculations of AlCp structures showed that the aluminium ligand bonds within the larger clusters were quite strong (on the order of 60 kcal/mol) and the most likely unimolecular thermal decomposition pathway would in fact be loss of AlCp units [6]. To further explore the stability and decomposition of these materials, we performed Car-Parrinello quantum molecular dynamics (CPMD) simulations of the structure,



thermodynamics, and oxygen stability of these compounds with a particular focus on their possible role as combusting fuels or propellants. We examined their thermal stability at 300K and 1000K with and without an oxygen shell of 36 O<sub>2</sub> molecules. We primarily considered four AlCp isolated clusters (figure 1): Al<sub>4</sub>Cp<sub>4</sub><sup>\*</sup>, Al<sub>4</sub>Cp<sub>4</sub>, Al<sub>50</sub>Cp<sub>12</sub><sup>\*</sup>, and Al<sub>50</sub>Cp<sub>12</sub>, all of which (save the unmethylated Al<sub>50</sub> compound) have been directly observed experimentally [7–9]. The simulations were performed in the NVE ensemble for equilibration for at least 5 ps for all clusters. After equilibration, we carried out these simulations in the NVT ensemble. An oxygen shell of 36 molecules were added to all clusters followed by a geometry optimization carried out on the oxygen shell only by constraining the geometry of all clusters. Structural measurements of all clusters after the 5 ps equilibration are in excellent agreement with original experimental measurements.



**Figure 1.** Equilibrated a) Al<sub>4</sub>Cp<sub>4</sub> b) Al<sub>4</sub>Cp<sub>4</sub><sup>\*</sup> c) Al<sub>50</sub>Cp<sub>12</sub> and d) Al<sub>50</sub>Cp<sub>12</sub><sup>\*</sup> clusters. Colors are, carbon (grey), hydrogen (white), and aluminum (magenta).

## 2. Computational Details

Molecular dynamics calculations were performed using a Car-Parrinello method as implemented in the CPMD code [10]. Electronic exchange and correlation effects were treated within the GGA in the PBE parameterization [11, 12]. Interactions between the nuclei and electrons are described with Vanderbilt ultra-soft pseudopotentials and a plane wave basis set with 25 Ry cut-off energy. Simulations were performed in the NVE ensemble for equilibration for at least

**Table 1.** Calculated structural measurements of  $\text{Al}_4\text{Cp}_4$  cluster after 5 ps equilibration compared to the average experimental measurements.

Bond type	Average theoretical bond length (Å)	Experimental (Å) <sup>1</sup>
Al-Al	2.86	2.77
Al-Cp	2.39	2.32
$\text{C}_{cp}\text{-C}_{cp}$	1.42	1.42
$\text{C}_{cp}\text{-C}_{Me}$	1.50	1.49
$\text{C}_{Me}\text{-H}$	1.05	0.98

<sup>1</sup>Experimental bond length [9]

5 ps and followed by NVT ensemble with Nose-Hoover thermostats and a thermostat frequency  $2800\text{ cm}^{-1}$ . Total simulation time of 7 ps beyond equilibration were enough to explore all surface oxidation and reduction reactions of  $\text{Al}_4\text{Cp}_4$ ,  $\text{Al}_4\text{Cp}_4^*$ , and  $\text{Al}_{50}\text{Cp}_{12}$  clusters. In the case of methylated  $\text{Al}_{50}\text{Cp}_{12}^*$  cluster, we increased the simulation time to 8.7 ps in order to explore these reactions. A small time step of 6 a.u. ( 0.15 fs) is used for the integration of equations of motion with 800 amu ( $\mu$ ) for the fictitious electronic mass. The computational parameters have been carefully chosen to obtain converged solutions to the Kohn-Sham equations. Non-periodic boundary conditions were used for all clusters.

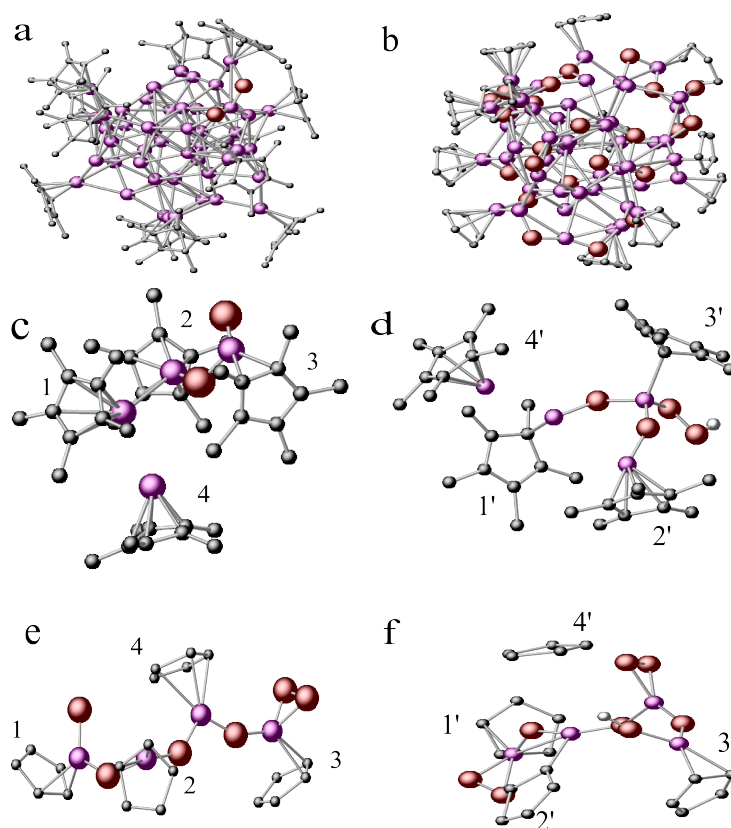
### 3. Results and Discussion

Structural measurements of all clusters after the 5 ps equilibration are in excellent agreement with available experimental x-ray diffraction measurements. Table 1 shows example structural measurements of  $\text{Al}_4\text{Cp}_4^*$  as compared to the solid-state diffraction values.

Overall, we observe minimal reaction between the oxygen and the ligand in our molecular dynamics simulations. In all cases, oxygen diffuses through the ligand layer, splits into atomic oxygen upon contact with the aluminium core, and then quickly reorients itself into a coordination motif reminiscent of  $\text{Al}_2\text{O}_3$ . Non-methylated clusters, with their reduced steric hindrance, are highly reactive and oxygen quickly diffuses into their core as would be expected.  $\text{Al}_4\text{Cp}_4$  and  $\text{Al}_4\text{Cp}_4^*$  are completely decomposed at high temperature into small aluminium-oxide type clusters with ligands still attached to the majority of aluminum. In the larger clusters, there is a clear steric hindrance effect between the methylated  $\text{Al}_{50}\text{Cp}_{12}^*$  and the non-methylated  $\text{Al}_{50}\text{Cp}_{12}$  cluster, but both show similar chemical pathways. Our previous calculations had suggested that loss of AlCp units was the most likely initial thermal decomposition step based on bond energies, but we see no evidence of this manner of decomposition in the quantum molecular dynamics simulations except in certain cases after oxidation has already occurred.

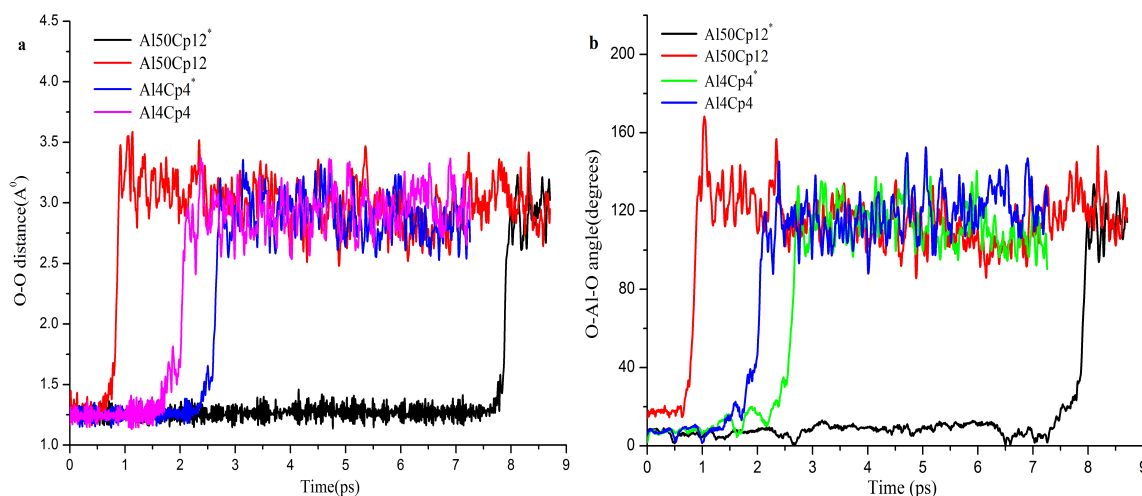
In the small  $\text{Al}_4$  clusters, oxygen molecules diffuse and interact with Al core directly after 2 ps of simulation time at 500K and 1000K. By 6 ps, these clusters have begun to unravel into an oxidized core with three remaining attached ligands. In both cases the Al oxidation process is followed by a hydrogen detachment from the Cp ligand groups. The main difference between these two cases is the final product; in the non-methylated cluster at least one ligand group detaches at the end of the oxidation process. In the methylated cluster an Al-Cp ligand group detaches towards the end of the simulation run. Figure 2 shows snapshots of all clusters following these initial oxidation reactions. All hydrogen atoms, except those that detached at the end of oxidation process in  $\text{Al}_4\text{Cp}_4$  and  $\text{Al}_4\text{Cp}_4^*$  clusters, are removed for better visualization.

For the larger  $\text{Al}_{50}$  clusters, multiple oxidation events are observed in which  $\text{O}_2$  diffuses through the protective ligand layer, separates into atomic oxygen, and continues to diffuse inside the core. None of the ligand groups detach during the process; rather, the clusters continue to swell with oxygen and equilibrate into new configurations. Even in cases where the oxygen



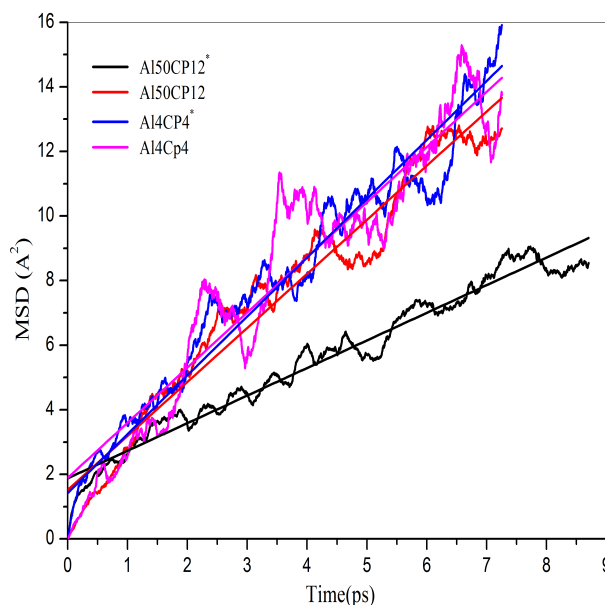
**Figure 2.** Simulation snapshots of a)  $\text{Al}_{50}\text{Cp}_{12}^*$  and b)  $\text{Al}_{50}\text{Cp}_{12}$  at the end of the simulation, c)  $\text{Al}_4\text{Cp}_4^*$  at earlier simulation time d)  $\text{Al}_4\text{Cp}_4^*$  at the end of the simulation, and e)  $\text{Al}_4\text{Cp}_4$  at earlier simulation time f)  $\text{Al}_4\text{Cp}_4$  at the end of the simulation. Colors are, oxygen (red), carbon (grey), hydrogen (white), and aluminum (magenta).

diffuses directly next to an Al-Cp bond (see figure 2), we do not observe loss of ligand units. No hydrogen detachment was observed in these larger clusters.



**Figure 3.** The dynamics of a) O-O bond length b) O-Al-O angle along the simulation trajectory. Finally, we consider an approximate means of quantifying the protective nature of the outer

ligand layer. In figure 3 we present the average oxygen separation in the first O<sub>2</sub> molecule to react with the cluster, as well as the average O-Al-O angle which formed directly after the splitting of this oxygen molecule. The separation and angle quickly approach values similar to that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. We define an effective diffusion constant for the oxygen moving through the protective ligand barrier based on the MSD, as shown in figure 4.



**Figure 4.** Mean square displacement of all clusters as a function of simulation time.

The effective diffusion constant can be calculated from the MSD as a function of simulation time and using the Einstein relation [13]:

$$\lim_{t \rightarrow +\infty} \langle |r(t+t') - r(t')|^2 \rangle = 6Dt$$

where  $r(t)$  is the displacement at time  $t$  and  $t+t'$  and  $D$  is the effective diffusion constant. The calculated diffusion constants of Al<sub>4</sub>Cp<sub>4</sub><sup>\*</sup>, Al<sub>4</sub>Cp<sub>4</sub>, Al<sub>50</sub>Cp<sub>12</sub>, and Al<sub>50</sub>Cp<sub>12</sub><sup>\*</sup> clusters are 2.85, 3.04, 2.79, and 1.42 (10<sup>-9</sup> m<sup>2</sup>/s) respectively. While our simulation time is not sufficient to establish true, reliable transport parameters, this appears to be a useful fast metric for comparison of the cluster's steric barrier. Al<sub>50</sub>Cp<sub>12</sub><sup>\*</sup> with its dense layer of surrounding methylated ligands has the lowest effective barrier diffusion constant of any Al-Cp system considered here. The Al<sub>50</sub>Cp<sub>12</sub> cluster is the fastest to react with oxygen as shown in figure 3. This behavior is a combination of the reduced steric barrier and the increased size of the Al core of this cluster. As would be expected, in Al<sub>50</sub>Cp<sub>12</sub> the oxygen molecules experience reduced interactions with ligand groups compared to the methylated Al<sub>50</sub>Cp<sub>12</sub><sup>\*</sup>. Hence, the steric barrier is lower in this cluster and oxygen diffuses faster through protective ligands. The larger Al core in the Al<sub>50</sub>Cp<sub>12</sub> cluster also provides more reaction sites for oxygen as compared to the small clusters. As a result, the probability of an oxygen molecule to diffuse and react with surface Al is larger in Al<sub>50</sub>Cp<sub>12</sub> compared to all other systems. Correspondingly, the effective diffusion constant is larger in this case, and is comparable to the Al<sub>4</sub> systems. Current work is ongoing to map out the energy profile of a diffusing oxidizer molecule using metadynamics combined with large Car-Parrinello simulations.

#### 4. Conclusions

We have performed Car-Parrinello simulations of the initial oxidation reactions of aluminum-cyclopentadienyl clusters being considered for energetics applications. The simulations indicate that ligand/oxygen interactions are minimal, and show no evidence of initial loss of aluminum-ligand units as would be expected from a simple analysis of bond strengths. Rather, the oxygen molecules diffuse through the outer steric barrier of the ligands, split into atomic oxygen after coming into contact with the aluminum cluster, and quickly reorient to a form similar to  $\text{Al}_2\text{O}_3$  (figure 3). An effective diffusion coefficient was calculated for  $\text{O}_2$  moving through the ligand layer, and appears to be a reasonable way to quantify the degree of steric protection offered by a particular ligand. In addition to the steric barrier effect of the protective ligand, the size of the Al core and hence the available sites for reaction play a significant role in the reactivity of these clusters. These simulations offer a means to quantitatively compare between ligand systems to gain a rough idea of the air stability of small metallic clusters.

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