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Ab initio metadynamics simulations of oxygen/ligand interactions in organoaluminum clusters

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Car-Parrinello molecular dynamics combined with a metadynamics algorithm is used to study the initial interaction of O_2 with the low-valence organoaluminum clusters Al_4Cp_4 ($Cp=C_5H_5$) and $Al_4Cp_4^*$ ($Cp^*=C_5[CH_3]_5$). Prior to reaction with the aluminum core, simulations suggest that the oxygen undergoes a hindered crossing of the steric barrier presented by the outer ligand monolayer. A combination of two collective variables based on aluminum/oxygen distance and lateral oxygen displacement was found to produce distinct reactant, product, and transition states for this process. In the methylated cluster with Cp^* ligands, a broad transition state of 45 kJ/mol was observed due to direct steric interactions with the ligand groups and considerable oxygen reorientation. In the non-methylated cluster the ligands distort away from the oxidizer, resulting in a barrier of roughly 34 kJ/mol with minimal O_2 reorientation. A study of the oxygen/cluster system fixed in a triplet multiplicity suggests that the spin state does not affect the initial steric interaction with the ligands. The metadynamics approach appears to be a promising means of analyzing the initial steps of such oxidation reactions for ligand-protected clusters. [http://dx.doi.org/10.1063/1.4897256]

I. INTRODUCTION

Small aluminum clusters have been extensively studied both experimentally and theoretically for many decades.[1–8] Certain small clusters, such as Al_{13}^-, show a surprising resistance to reaction with O_2; this has been attributed to the electronic stability of the cluster due a complete filling of jellium orbitals, as well as the spin-forbidden reaction between triplet O_2 and the singlet aluminum cluster.[9–12] Recent experimental advancements have made direct study of single-collision oxygen interaction with aluminum clusters possible in ultra-high vacuum conditions, allowing estimates of rates and reaction products for the initial chemical steps of cluster oxidation.[9,12] Neumaier *et al.* explore the spin-forbidden reactions of aluminum and gallium clusters in recent work, and conclude that a peroxo-intermediate state is key in determining Al_x^- ($x = 9$–14) reaction rates with a single oxygen molecule.[12] The rate variation observed for open- and closed-shell Al and Ga clusters confirms the importance of the spin-forbidden interaction with O_2 and demonstrated increased reactions rates for Al compared to Ga. Their method shows the feasibility of studying oxidation of size-selected gas phase clusters at a scale that can be directly compared to quantum simulations. This opens up the possibility of studying oxygen interactions in a wide range of other small cluster materials.

While bare aluminum clusters have received considerable attention in the literature, synthesis efforts by Schnöckel and co-workers over the last three decades have resulted in a range of ligated organoaluminum clusters that also possess unique electronic and structural properties.[13–17] Aluminum(I) halide solutions have been used as precursors to form a variety of organoaluminum complexes such as $Al_4Cp_4^*$.

Here Cp^* refers to the fully methylated cyclopentadienyl ligand ($Cp^*=C_5[CH_3]_5$) and Cp to the non-methylated form ($Cp=C_5H_5$). The final oxidation state of aluminum in these clusters is typically below 3. In certain cases, further disproportionation reactions can lead to formation of large metalloid clusters such as $Al_{50}Cp_{12}^*$ and $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$.[14,17] Recent theoretical analysis has suggested that these may also be analyzed with a modified jellium model, and that the observed organoaluminum clusters such as $Al_4Cp_4^*$ may represent stable magic-number forms.[18,19] This may result in hindered reactions with O_2 due both to electronic structure effects as well as the physical steric barrier of the ligands surrounding the metal core. The oxidation kinetics and high energy density of these systems are also of interest for possible applications in hydrogen production from water[20,21] or as fuel additives.[22,23] A range of similar ligand-protected clusters are also known; ligated gold clusters in particular have received considerable attention in recent years.[25–29]

Recently we have performed *ab initio* molecular dynamics simulations to examine the interaction of oxygen with four prototypical organoaluminum clusters: Al_4Cp_4, $Al_4Cp_4^*$, $Al_{50}Cp_{12}$, and $Al_{50}Cp_{12}^*$, as an initial investigation of their reaction pathways and the onset of chemistry.[23,24] Due to the fixed multiplicity and the large sizes of the simulated systems, the oxygen was kept in the singlet state. We found that the initial reaction steps were physical, not chemical; in all cases there was an initial motion of the O_2 through the steric barrier of the ligand, followed by a chemical splitting of oxygen at the cluster core and the formation of Al/O clusters with coordination motifs similar to those in aluminum(III) oxides. The aluminum/ligand bonds remained intact during this initial physical barrier crossing. Chemical reactions between the oxygen and ligands were not generally observed, but a significant qualitative difference between methylated (Cp^*) and

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non-methylated (Cp) clusters was observed due to the large difference in steric hindrance. These simulations are computationally intensive, and require high temperatures and a considerable quantity of oxygen in close proximity to the cluster in order to observe relevant chemistry on the scale of *ab initio* molecular dynamics (<10 ps). Additionally, it is desirable to extract a quantifiable metric for the initial physical interaction between the oxygen and the ligand as a means of comparing the stability of various ligated aluminum clusters.

In order to further study this initial physical process of O₂'s hindered crossing of the ligand steric barrier, we here report metadynamics (MTD) simulations in which a biasing potential is used to accelerate the barrier crossing and examine it in a short *ab initio* molecular dynamics trajectory. The metadynamics technique is an efficient way to study rare events based on combining a coarse graining of the dynamics with a time-dependent bias potential.[30,31] Reliable simulations using this method, however, require careful choice of a small number of arbitrary collective variables that must properly account for the slow processes of interest. Here a method is developed to provide a means of estimating the energy barrier in a computationally efficient way. Our goal is to develop a general metadynamics approach that can ultimately be applied to study these physical barrier crossings in a range of organoaluminum clusters, including those with significant steric bulk in their ligand groups.

Car-Parrinello (CPMD) simulations are used with a small number of metadynamics collective variables to study the free energy landscape of one oxygen molecule interacting with the steric barrier of organoaluminum Al_4Cp_4 and $Al_4Cp_4^*$ clusters. Different behavior was observed in each cluster; in the methylated system with Cp* ligands, a broad energy barrier was observed due to direct steric interactions with the ligand groups. Considerable oxygen reorientation is observed during this process, and the overall energy barrier is approximately 45 kJ/mol. In the non-methylated Cp system, the initial process involved distortion of the ligands away from the oxidizer, a barrier of roughly 34 kJ/mol. A simple collective variable based on the aluminum/oxygen distance produces a distinct barrier on the free energy surface, but the addition of a second variable to allow lateral displacements of the oxygen was found to improve exploration of nearby minima for cases where significant steric hindrance induces oxygen reorientation. A study of the oxygen/cluster system fixed in a triplet multiplicity suggests that the spin state does not affect the initial interaction with the ligand, though it is expected to play a role in the eventual oxidation chemistry.

II. COMPUTATIONAL METHODOLOGY

Within the metadynamics algorithm, a set of collective variables (CV) S_α representing functions of the reaction coordinates is introduced to describe the dynamics in the CV's space. Because these variables describe slow processes, they can be treated separately from the other variables in the system. A new set of variables s_α associated with S_α is used to describe these dynamics. A history dependent potential, constructed as a sum of Gaussians centered at the trajectory, is introduced to discourage the system from visiting the same

points along the reaction coordinates.[32–34] In terms of these new variables, the system can be described by the extended Lagrangian

$$\mathcal{L} = \mathcal{L}_{CP} + \sum_\alpha \frac{1}{2} M_\alpha \dot{s}_\alpha^2$$
$$- \sum_\alpha \frac{1}{2} K_\alpha [S_\alpha(R_I) - s_\alpha]^2 + V(t, s), \qquad (1)$$

where $\mathcal{L}_{CP}$ is the Car-Parrinello Lagrangian, M_α and K_α are the fictitious mass and the coupling constant for the harmonic potential assigned for each variable s_α, and $V(t, s)$ is the added time dependent potential in the form of Gaussian hills and given by

$$V(t, s) = \sum_{t_i < t} w_i \exp\left[-\frac{(s - s^i)^2}{2(\Delta s^\perp)^2}\right]$$
$$\times \exp\left[-\frac{((s^{i+1} - s^i).(s - s^i))^2}{2(\Delta s_i^\parallel)^4}\right]. \qquad (2)$$

The hill widths, $\Delta s^\perp$ and the hills heights, W_i are parameters that affect the ability of the system to escape from local minima. For the molecular dynamics, the electronic exchange and correlation effects were treated with a PBE functional[35] and all simulations were performed with the code CPMD.[36] Interactions between the nuclei and electrons were described with Vanderbilt ultrasoft pseudopotentials and a plane wave basis set with a 25 Ry cut-off energy. Isolated clusters were initially equilibrated in an NVE ensemble for 5 ps. The oxygen was then added and a geometry optimization was performed to allow it to reorient into a stable starting configuration outside the ligand shell. The molecular dynamic simulations themselves were performed in an NVT ensemble with a Nose-Hoover thermostat of frequency 2600 cm⁻¹ and 1000 K average temperature. A fictitious mass of 400 amu was used, allowing a time step of 4 a.u. (~0.08 fs) for the integration of the equations of motion. Non-periodic boundary conditions were used in the Poisson solver for all clusters.

We next consider the metadynamics parameters, an essential component in ensuring that the full free energy surface is sampled during a trajectory. The masses of the CVs (M_α) were set to 40 amu and 2.3 for the coupling constants (K_α). M_α and K_α were chosen such the maximum value of the harmonic term in the Lagrangian (Eq. (1)) was on the order of 10 kJ/mol for these simulations. The heights of the Gaussian-like hills were set to a minimum of 1.0 kJ/mol, a maximum of 10.5 kJ/mol, and an average of 5.2 kJ/mol. The hill width $\Delta s^\perp$ was set to 0.2 and the normal $\Delta s_i^\parallel$ fluctuated in the interval [0.01:0.05]. New hills were added to this system at a minimum time separation of 15 MD steps and maximum time separation of 25 MD steps with a displacement check equal to half the width of the Gaussian hills. This procedure results in smooth free energy surfaces and well defined reactant, product, and transition state configurations. Multiple metadynamics trajectories were run from the initial starting points to ensure that the free energy profiles were consistent. The acceleration from the MTD algorithm allowed the full energy profile of the main barrier crossing process to be sampled in a

short run (approximately 1 ps). We note that starting geometries of the O_2 very far from the optimized configuration will result in different energy barriers if used with these identical metadynamics parameters; in such cases additional time is needed for the O_2 to equilibrate before beginning the barrier crossing. Optimizing the O_2 in the manner described above was found to give repeatable energy barriers with a variation on the order of ~4 kJ/mol.

III. RESULTS AND DISCUSSION

The choice of appropriate CVs is crucial in order to reconstruct an accurate free energy surface. We begin with the simplest case, that of a one-dimensional free energy pathway using only the Al-O distance (D) as a collective variable. This is depicted in Figure 1, which shows the starting configuration of oxygen around the $Al_4Cp_4^*$ cluster. A second CV is later added to explore O_2 reorientation during the hindered barrier crossing through the ligand, but the key features of the process are prominent even with a simple aluminum/oxygen distance variable. The one-dimensional free energy profile of O_2 physically moving through the ligand layer of the $Al_4Cp_4^*$ system is shown in Figure 2. This figure also includes snapshots of the trajectory at representative points on the free energy surface.

The oxygen begins approximately 6 Å from the aluminum core, and an arbitrary zero-energy reference point is chosen at this starting position. Small energy barriers (~10 kJ/mol and below) are observed as it begins to approach the ligands, mainly arising from O_2 rotation and adjustment as it moves near the steric barrier of the methyl groups. Significant
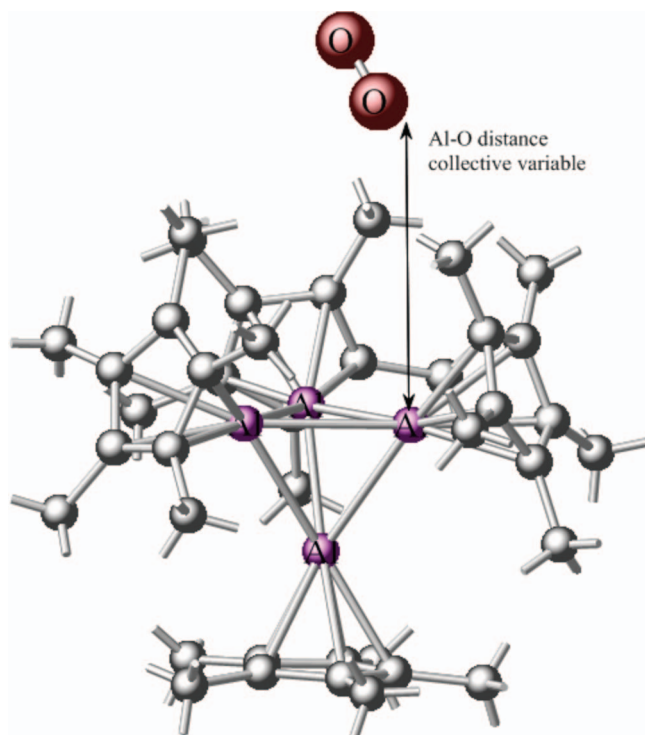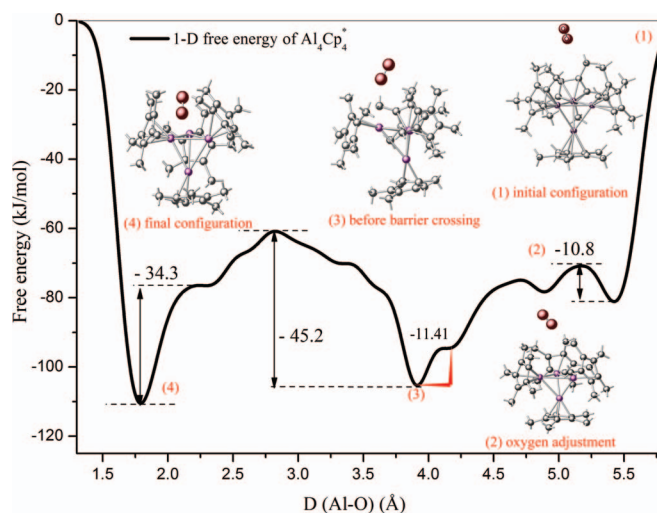

FIG. 2. 1-D free energy profile and structural evolution of the $Al_4Cp_4^* + O_2$ system along the trajectory, plotted in terms of the single Al-O distance.

reorientation of the oxygen is observed when using this single CV; we will return to this point again and expand to a second CV to more explicitly explore this dynamics. Following these initial transitions, the system moves into a deep energy minimum located at 3.9 Å. The main energy barrier for the process then follows, as the methyl groups are distorted during the barrier crossing. After a distinct 45 kJ/mol transition state, the oxygen moves into a stable configuration inside the cluster. The final energy of this state is similar to that before the steric barrier crossing, and the simulation is terminated at this point before the onset of chemistry. Previous *ab initio* molecular dynamics simulations showed that in most cases the oxygen quickly splits at the aluminum core and the cluster rapidly reorients once the O_2 moves through the ligand.[23]

The unmethylated Al_4Cp_4 system, with its considerably reduction in steric bulk, shows quantitatively different behavior during the hindered barrier crossing of oxygen. The free energy profile for this system is shown in Figure 3, also with snapshots taken from the trajectory. O_2 reorientation does not generally occur in this system. Rather, during the initial

FIG. 1. Al-O distance as a collective variable in both Al_4Cp_4 and $Al_4Cp_4^*$ systems. Colors are: carbon (grey), aluminum (magneta), and oxygen (red). Hydrogens are removed for better visualization.
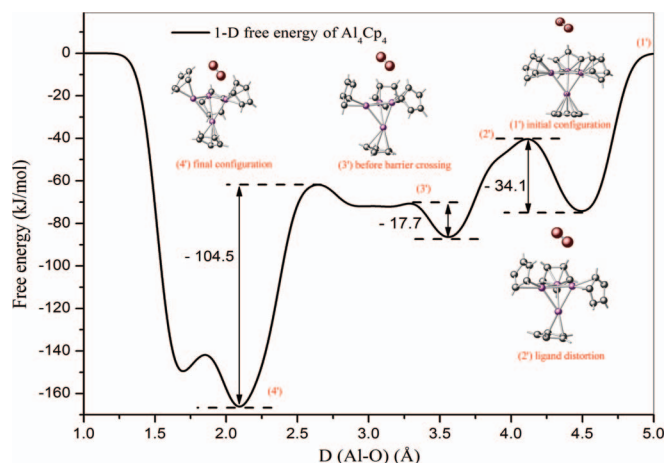

FIG. 3. 1-D free energy profile and structural evolution of the Al_4Cp_4 system along the trajectory.

approach there is a separate energy barrier (34.1 kJ/mol) which corresponds to distortion of the Cp ligands away from the O_2 molecule, a process that can proceed due to the absence of bulky methyl groups. As the oxygen moves closer to the core along the collective variable, no additional large energy barriers are observed. Distortions in AlCp units minimize interactions between O_2 and the ligands and the oxygen moves on a flatter energy surface. The distortion of the ligands continues as the Al/O distance is reduced, and ultimately the system evolves into a deep minimum with the oxygen close to the core and the ligands distorted away.

The features due to oxygen reorientation in the bulky methylated system suggest that additional slow dynamics may be present in this motion that need to be accounted for. The small barriers present between points (1) and (3) in the free energy surface in Figure 2 are due to O_2 reorientation as the molecule interacts with the methyl groups. These reorientations are absent in the unmethylated cluster. Our ultimate aim is to develop a metadynamics methodology that allows us to examine this physical barrier crossing for a wide range of ligand-stabilized aluminum clusters, some of which may have considerable steric bulk (such as the experimentally known $Al_4[Si(t\text{-}Bu)_3]_4$). In order to keep the computational algorithm tractable for future studies considering a range of ligands, we cannot introduce a large number of collective variables. Hence, we want a second CV in addition to the Al-O distance that will account for a range of orthogonal motions in the oxygen that the system may experience when bulky ligands are present.

To further probe the ligand steric interactions and ensure that the use of Al-O distance collective variable produced reasonable results, we introduced a second simultaneous collective variable which represents the average displacement of O_2 along a particular plane. The displacement, given as a length, represents the total displacement along this specified plane since the last Gaussian in this collective variable was added. The plane is chosen as follows. Both clusters were placed within a cubic unit cell 30 Å on a side and their center of mass placed at the middle of the cell. The (111) plane was chosen within this cell, with the clusters oriented as shown in Figure 4. The plane roughly bisects the cluster and passes near to the starting point of oxygen outside the ligand. We note that the molecule is not constrained to move in this plane, simply that the bias potential acts along this surface. The choice of this second collective variable is to bias the system to fully explore reorientation of the O_2 during the barrier crossing. This is expected to be particularly important for bulky ligands, where there may be additional minima on the free energy surface not captured by a simple aluminum/oxygen distance.

The two-dimensional free energy maps of both systems, in the space of these two collective variables, are shown in Figure 5. We begin with the methylated $Al_4Cp_4^*$ system shown in Fig. 5(a). In this case, the additional CV allows the system to explore a different energy pathway as the O_2 approaches the main barrier crossing. The system begins at point (a), and the initial pathway from (a) to (b) is very similar to the 1D scenario with a 10.5 kJ/mol energy barrier and minimal displacement along the second CV. Around 4.25 Å from the aluminum (point (b)), the second collective variable aids in
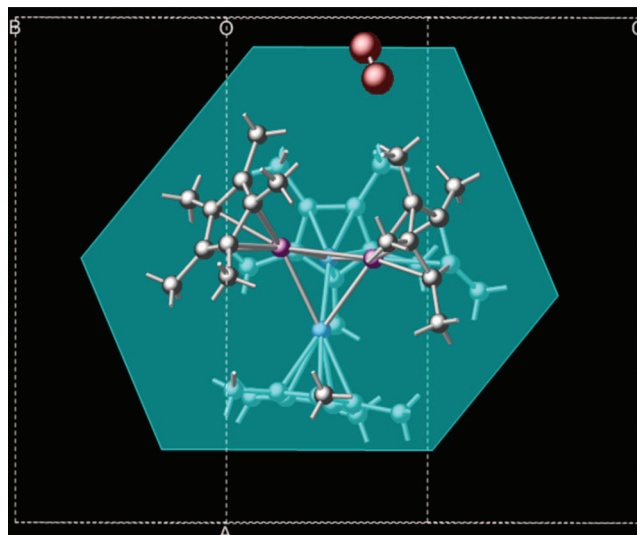

FIG. 4. The plane defined for O_2 displacement with respect to Al, used as a second collective variable to explore the barrier crossing.

displacing the oxygen molecule and exploring a lower energy pathway that leads to a new minimum energy state (c) at 3.75 Å. The energy barrier for this transition is 25.5 kJ/mol. Red arrows in Figure 2 mark a signature of this additional minimum in the 1D free energy surface, a feature that could not be adequately explored when using the aluminum/oxygen distance alone. From here the system undergoes the main barrier crossing through the methyl groups, but from this transition state the remaining barrier is only 18 kJ/mol. The O_2 then proceeds to the product basin near the aluminum atoms where the oxidation reaction is expected to begin (d). We note that the total energy barrier for both events is 43.5 kJ/mol, extremely close to the 1D case; the main additional information is the presence of a separate minimum as the oxygen is displaced and reorients itself around the ligand.

The unmethylated Al_4Cp_4, shown in Figure 5(b), does not show a prominent effect from the additional CV. An initial energy barrier remains as a result of ligand distortion as the system moves from point (a′) to (b′); the total barrier is 35.7 kJ/mol compared with 34.1 kJ/mol for a single collective variable. The displacement collective variable remains close to zero along most of the energy pathway, and the main barrier crossing at (c′) retains a relatively low energy (13.1 kJ/mol) which is very similar to that in the one-dimensional case (17.1 kcal/mol). Once in close proximity to the cluster, the second CV does result in a more complex product basin (d′), as the oxygen begins to reorient and chemically react when close to the core.

Due to the extremely complex chemistry involved in the growth of these metalloid clusters in solution, it is likely unwarranted to assume larger ligands with greatly enhanced sterics would still form systems with metal cores of identical symmetry. The exact growth mechanism of these clusters is unknown, but has been hypothesized to involve insertion reactions of aluminum/ligand units and elimination of trivalent species.[8] Enhanced ligand bulk may alter this process as well. Interestingly, many of the largest known Ga and Al metalloid systems have a dense network of steric interactions
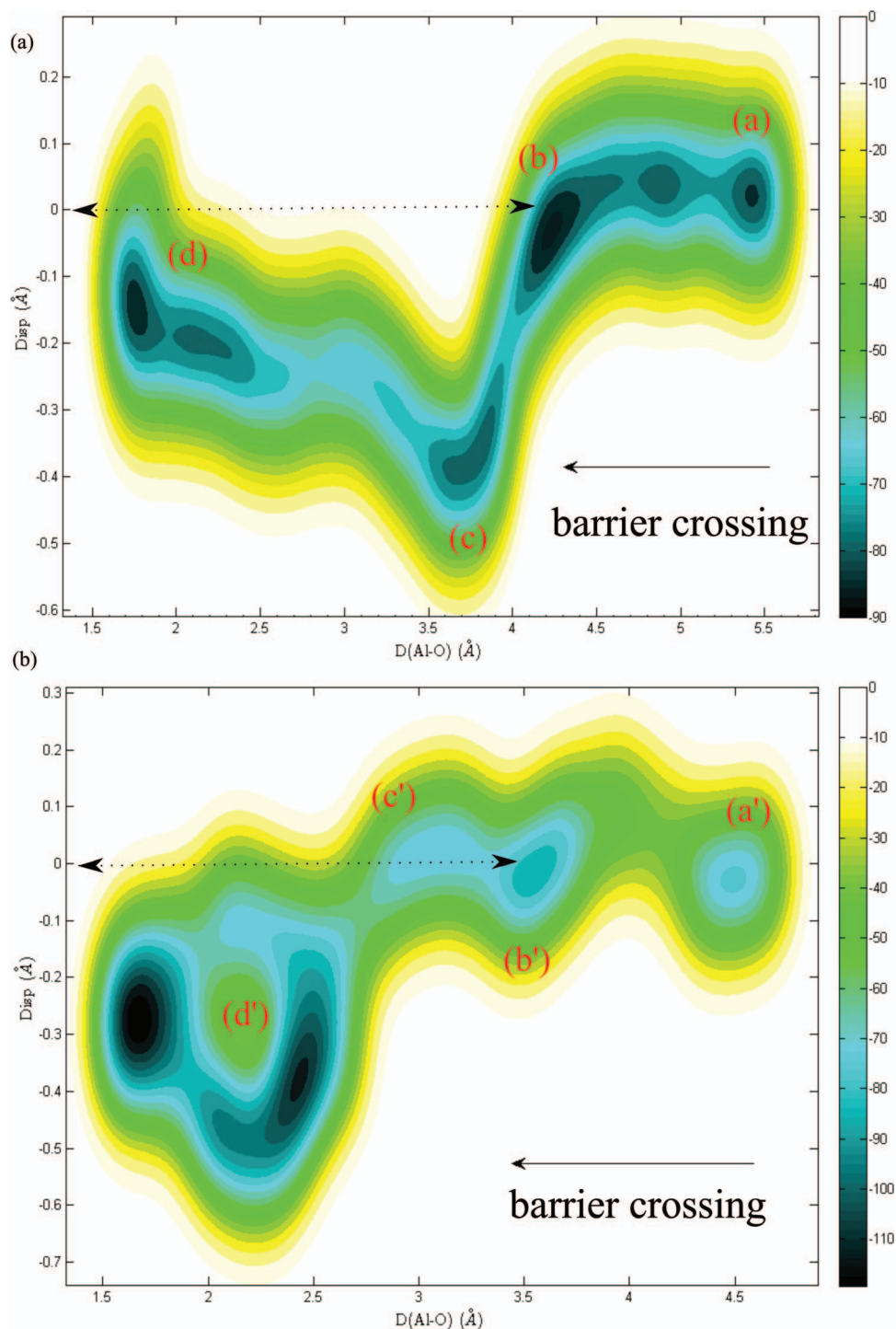
FIG. 5. 2-D free energy profiles of O_2 interaction with the (a) $Al_4Cp_4^*$ and (b) Al_4Cp_4 systems. Dashed lines indicate of zero displacement in the second collective variable.

between exterior ligands.[8] This may play a role in stabilizing the electronic structure of the system, as well as kinetically trapping the cluster by limiting further insertion reactions. While ligands with additional bulk parallel to the aluminum/ligand bond are desirable to improve air stability and the O_2 steric barrier discussed here, the growth process and potential for cluster formation may be greatly altered in this case.

We note that the steric energy barriers here are comparable to the bonding energy of the tetramers. Our previous calculations gave bond dissociation energies of 62.9 kJ/mol for Al_4Cp_4 and 30.9 kJ/mol for $Al_4Cp_4^*$; in both cases the energy is for the tetramer breaking into four aluminum/ligand monomers.[22] Stable dimer or trimer configurations have not been found for the AlCp or AlCp* units. Thus we might expect that for the tetramers considered here, O_2 will be readily available to the interior aluminum core and may not require initial decomposition of the ligand or removal of an AlCp unit. What these simulations cannot directly address, however, is an additional barrier for a spin-flip process that would likely
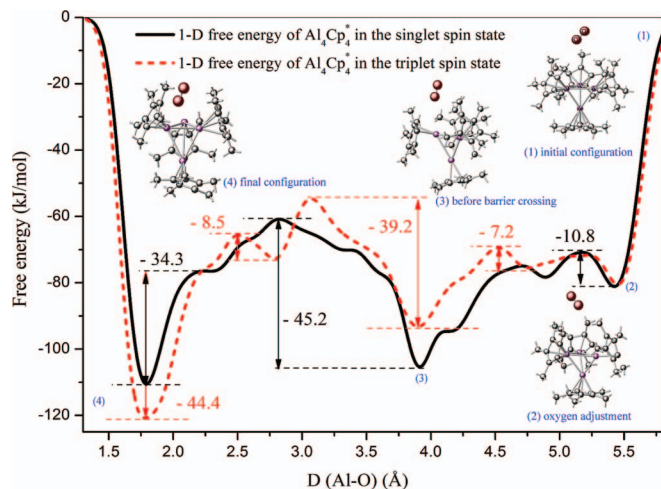
FIG. 6. 1-D free energy profile of the $Al_4Cp_4^*$ system in the singlet (solid line) and triplet (dashed line) spin states. Snapshots represent the structural evolution of the $Al_4Cp_4^*$ system in the triplet spin state along the dynamics trajectory.

precede the oxidation of the cluster. We briefly consider this situation next.

The proper ground state of oxygen is a triplet, which introduces many complexities due to the spin-forbidden nature of the O_2 reaction with the cluster. The spin state is quenched to a singlet state during adsorption or interaction of ambient oxygen with an Al surface, leading to a non-trivial spin-flip process that cannot be easily accounted for with traditional *ab initio* molecular dynamics.[37–39] We cannot easily treat the crossing between singlet and triplet barriers, and thus the simulations discussed up to this point have used singlet oxygen. A natural question, however, is whether an initial triplet oxygen spin state affects the physical barrier crossing that precedes the chemical reaction. To address this issue, we carried out the same one-dimensional simulations for the $Al_4Cp_4^*$ system but with a triplet multiplicity enforced for the overall system. The $Al_4Cp_4^*$ system was fully optimized in both singlet and triplet spin states at the beginning of these simulations. We found an approximately 78 kJ/mol energy difference between these initial states in favor of the triplet. The free energy profile in 1D using the Al-O distance as a collective variable is shown in Figure 6, along with snapshots of the clusters. The singlet surface from Figure 2 is also repeated for comparison. Metadynamics parameters were identical in both simulations and both were normalized to zero energy at a distance of 6 Å.

The barrier crossing is very consistent for both multiplicities, except for small variations along the reaction coordinate. The diffusion begins at the same aluminum/oxygen distance (3.9 Å), and the primary energy barrier due to the ligand is within 6 kJ/mol of the singlet case (39.2 kJ/mol triplet versus 45.2 kJ/mol singlet). The motion of the oxygen and nearby ligands is similar for both multiplicities. While the spin-flip transition will likely have a significant effect on the oxidation at later times, the metadynamics simulations here suggest that the multiplicity does not play a major role in the initial physical process of the ligand barrier crossing.

IV. CONCLUSIONS

In conclusion, we have performed Car-Parrinello quantum molecular dynamics simulations of the hindered barrier crossing of oxygen as it interacts with two prototypical organoaluminum clusters, $Al_4Cp_4^*$ and Al_4Cp_4. For the purposes of these simulations, these clusters differ primarily in the steric barrier their ligands present to an oxidizer. A metadynamics algorithm was used to accelerate the barrier crossing process to be observable in a short *ab initio* molecular dynamics simulation, and to extract key energy barriers during the event. These systems allow us to establish a computational methodology for studying the initial physical barrier crossing as oxygen interacts with small ligand-stabilized aluminum clusters, before the onset of chemistry. Different behavior was observed in each cluster; in the methylated system with Cp* ligands, a broad energy barrier was observed due to direct steric interactions with the ligand groups. Considerable oxygen reorientation is observed during this process, and the overall energy barrier is approximately 45 kJ/mol. In the non-methylated Cp system, the initial process involved distortion of the ligands away from the oxidizer, a barrier of roughly 34 kJ/mol. A simple collective variable based on the aluminum/oxygen distance produces a distinct barrier on the free energy surface, but the addition of a second variable to allow lateral displacements of the oxygen was found to improve exploration of nearby minima for cases where significant steric hindrance induces oxygen motion. A study of the oxygen/cluster system fixed in a triplet multiplicity suggests that the spin state does not affect the initial interaction with the ligand, though it is expected to play a role in the eventual oxidation chemistry. These results suggest that a metadynamics approach is promising for comparing the steric barriers of ligand-stabilized metal clusters in a computationally efficient manner.

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