I. Introduction

The dissociative adsorption of oxygen on metal particles and surfaces is very important for heterogeneous catalysis and material processing, both of tremendous technological importance. However, whereas for the interaction of O$_2$ with transition metal surfaces, the microscopic reaction mechanism seems to be fairly well understood, there are still some open questions left. Concerning the dissociative adsorption of O$_2$ on Al(111), molecular beam results indicate some adsorption hindrance attributed to a small barrier.

There have been various attempts to theoretically describe this hindrance because standard electronically adiabatic periodic DFT calculation found that the dissociation of O$_2$ on Al(111) is not hindered by any barrier; that is, the adsorption should occur spontaneously, in contrast to the experiment. Recently, it was shown that the low sticking probability for thermal O$_2$ molecules impinging on Al(111) could be explained by assuming diabatic approach of O$_2$ in its gas-phase triplet state without adiabatically switching to a singlet state near the surface. This explanation has been supported by the observation of spin-selection rules in the interaction of O$_2$ with small Al anion clusters ($\sim 10-20$ atoms), leading to an odd/even pattern in the reactivity with O$_2$ as a function of the number of atoms, $n$, in the Al clusters.

On the other hand, there have also been several other calculations, independently motivated, that provide some information about the behavior of the local environment of aluminum atoms on various adsorbents. For example, O$_2$ around an Al$_6$ cluster seems to interact somehow with apex Al atoms before eventual adsorption on the cluster, also, structural deformation of surface aluminum atoms on alumina clusters causes a steric hindrance in the adsorption of NH$_3$ molecule. These direct us to examine the possibility of steric hindrance in the adsorption of O$_2$ on the Al(111) surface.

In a recent paper, the reactivity of O$_2$ ($\Sigma_g^-$) with planar Al$_4$ clusters was investigated at both the multireference configuration interaction (MRCI) and the density functional theory (DFT) levels. The motivation for that study was the question about the existence of an activation barrier in the adsorption of O$_2$ on an Al crystal. A comparison of the results of these two methods can be accomplished only in systems of small Al clusters in which the MRCI calculations can be applied. The MRCI calculations on the interaction of O$_2$ with a small Al$_4$ cluster did yield a barrier of $\sim 13$ kcal/mol for the square cluster geometry $\Gamma A_4$ and about 6 kcal/mol for the rhombus geometry $\Gamma A_2$, with the O--O axis parallel to the cluster plane. In addition, these MRCI calculations indicated a dissociative adsorption when the O--O axis was vertical to the square cluster plane. Similar findings were obtained by Livshits et al., who addressed the O$_2$ dissociation on Al$_4$ clusters using hybrid DFT functionals.

The DFT results showed a lack of any barrier either in the parallel or in the vertical O--O approach, which was assumed to be an artifact of the improper description of many-body effects in the employed GGA functionals. Hence, it was speculated that the absence of a minimum adsorption barrier in the periodic DFT calculations might be an artifact of the employed functionals so that there would be no need to invoke a nonadiabatic mechanism to explain the dissociative adsorption of O$_2$ on Al(111).

The adsorption on surfaces can be dominated by active sites that often correspond to defects; however, this is not necessarily always the case, as recently shown for early transition metal surfaces. To address the question whether for O$_2$ adsorption on Al the considerations discussed above also apply to defect sites, in the present work, we have explored the interaction of O$_2$ with a small Al$_4$ cluster in a tetrahedral geometry, when O$_2$ is parallel to the pyramid basis, employing both MRCI and DFT calculations and using a richer basis set than before. Thus, we also address the reliability of DFT with respect to the O$_2$/Al system. The calculations are not only helpful for the understanding of the interaction of O$_2$ with Al defect sites but should also be relevant as far as the adsorption of O$_2$ on small clusters is concerned.

Approaches under other angles (i.e. the largest part of phase space) are intricate and complex, involving pronounced orientational dependence, which opens up possibilities for molecular precursors and abstraction via intermediate molecularly chemisorbed states. A complete study of the potential energy surface is beyond the scope of this paper (and we doubt its success...
of the pyramid as a reference point, say, Al1, and this defines a reference basis of the pyramid as the basis opposite to Al1. We take Al1 as the origin of the coordinate system with the z-axis vertical to the basis and the y-axis parallel to a side of the basis. We add an oxygen molecule above Al1 so that the O−O center of mass lies on the z-axis; its distance from the origin is denoted by ρ. The O−O line is taken to be permanently parallel to the y-axis, and the O−O distance is denoted by r.

III. Calculations

We shall see that the potential energy surface (PES) cut of this geometry shows, by both MRCI and DFT, two energy minima, a shallow one above the apex Al1, which suggests the existence of a shallow energy trap, and a deeper one below Al1. We further investigate by DFT the actual existence of an upper energy trap by relaxing all oxygen coordinates (keeping the shape and size of the pyramid fixed). Indeed, it is seen that O2 binds slightly there, just above the apex Al1 atom, by orienting itself on a vertical mirror (σv) plane.

A. MRCI Calculations. For the MRCI calculations, we employed the MOLPRO package24 with the cc-pVTZ basis set of Dunning et al.25,26 For Al4 in the square and rhombus geometries, the calculations were done at the D2h symmetry with a self-consistent field (SCF) electron configuration of 16e on a1, 10e on b1g, 10e on b2g, 6e on b3g, 6e on b1u, 2e on b2u, and 2e on b3u orbitals for the X3 B1g and X3 A1g states. For a rectangle (D2b), the SCF electron configurations were 12e on a1, 4e on b1g, 10e on b2g, 6e on b3g, 2e on b1u, and 2e on b2u orbitals for the X3 B1g and X3 A1g states. For the Al4 cluster in tetrahedral geometry (Td), the calculations were done at the C1 symmetry with an SCF electron configuration of 36a′′, 16a′, 16a′′ electrons for A1′′, A2′, and 37a′′, 15a′′ electrons for X1A′′. At the multiconfiguration SCF (MCSCF) step, we employed a 12/10 reduced active space (RAS) of 12 electrons in 10 active orbitals. All the MRCI calculations were run using these reduced active space SCF (RASSCF) orbitals.

The calculations on the Al4 + O2 system were done at C1 symmetry so that all 68 electrons were in 35 orbitals of the same symmetry with two of them singly occupied. A 20/12 RAS was adopted at the MCSCF step, in which only the four 2p electrons on each O were included in the RAS. All the MRCI calculations were run using the RASSCF orbitals.

B. DFT Calculations. The DFT calculations on the Al4 + O2 system are done at C1 symmetry, so that all 68 electrons are in 35 Kohn−Sham orbitals of the same symmetry with the highest two of them singly occupied. We employed the Gaussian 03 package27 using the split-valence triple-ζ basis set 6-311+g* with polarization and diffuse functions28–30 and the Becke 3-parameter (exchange), Lee, Yang, and Parr (correlation) density functional (B3LYP).31–34

IV. Results and Discussion

For the MRCI calculations, we start the calculations at ρ = 5 Å (the distance of O2 from the apex Al1 atom) and r = 1.20 Å (the internuclear O−O distance) and proceed at smaller and smaller ρ. At each ρ, only r is optimized at the CI level by running MRCI calculations at intervals of Δr = 0.05 Å. The overall system is taken to be a triplet, the same as the ground state of the gas-phase O2.

The calculated PES cut is shown in Figure 2a, along with the curve of r, as functions of ρ. There is an activation barrier of ∼24 kcal/mol at ρ ≈ 3 Å and a plateau at around ρ ≈ 1 Å and r ≈ 2.7 Å, which is the length of the pyramid side. Hence, even for the approach toward a protruding atom, the adsorption

---

**TABLE 1: Optimized (by analytic gradient) MRCI Energy Differences from the Ground State, And Geometries, of Al4 Clusters in Different Structures in Their Lowest Singlet and Triplet States**

<table>
<thead>
<tr>
<th>Geometry</th>
<th>ΔE (kcal/mol)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>θ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>square singlet</td>
<td>4.838</td>
<td>2.630</td>
<td>2.630</td>
<td>90.0</td>
</tr>
<tr>
<td>square triplet</td>
<td>0.226</td>
<td>2.684</td>
<td>2.684</td>
<td>90.0</td>
</tr>
<tr>
<td>rhombus singlet</td>
<td>2.636</td>
<td>2.603</td>
<td>2.603</td>
<td>67.7</td>
</tr>
<tr>
<td>rhombus triplet</td>
<td>0</td>
<td>2.642</td>
<td>2.642</td>
<td>75.4</td>
</tr>
<tr>
<td>rectangular singlet</td>
<td>8.936</td>
<td>2.623</td>
<td>2.730</td>
<td>90.0</td>
</tr>
<tr>
<td>rectangular triplet</td>
<td>2.051</td>
<td>2.652</td>
<td>2.688</td>
<td>90.0</td>
</tr>
<tr>
<td>tetrahedral singlet</td>
<td>12.776</td>
<td>2.683</td>
<td>60.0</td>
<td></td>
</tr>
<tr>
<td>tetrahedral triplet</td>
<td>9.676</td>
<td>2.692</td>
<td>60.0</td>
<td></td>
</tr>
</tbody>
</table>

* a and b are the side lengths in Å, and θ is the angle between the sides in degrees.

---

**Figure 1.** Total MRCI energy differences of the considered MRCI-optimized Al4 cluster structures in the singlet (S) and triplet (T) state in kcal/mol with respect to the triplet rhombus geometry. RH, rhombus; SQ, square; REC, rectangular; TETR, tetrahedral geometries. For reference, the optimized MRCI energy of the ground state is −967.881 kcal/mol. The optimized MRCI energies of triplet rhombus and square are rather close to each other; this, of course, does not affect the rest of present work.
Figure 2. Graph of the PES cut of the Al₄ + O₂ under partial optimization of the O–O distance as O₂ attacks Al₄ along the z-axis, parallel to the pyramid basis. r is the O–O distance, and ρ is the Al₁–O₂ distance (see text). The plot of r as a function of ρ is also shown (right axis). (a) MRCI, (b) DFT results.

Figure 3. 3-D and contour diagram of the DFT potential energy (in a.u.) as O₂ approaches the top atom, apex of the Al₄ pyramid, for various O–O separations (in Å). The dashed line in the contour diagram, indicating the O–O bond opening, during the adsorption process, is also shown in Figure 2a and b. The energy separation of the contours is 0.01 a.u.

Figure 4. Isovalue plots of the spin-up (left panel) and spin-down (right panel) HOMO of the triplet state, around the first, most remote transition barrier at a distance of ρ ≈ 3 Å from the Al₁ atom, as O₂ approaches the top of the Al₄ pyramid. During the transition, O₂ attracts some electronic charge density from the cluster.

of O₂ on an Al cluster is activated; that is, such an adatom is not necessarily more active toward O₂ dissociation than Al atoms in a planar geometry. Since our MRCI calculations are quite accurate, we believe that the barrier at ρ ≈ 3 Å indeed exists.

We observe that the O–O bond opens as the oxygen approaches the apex of the pyramid from 1.2 to 3.3 Å at the apex (ρ = 0) and then diminishes slightly to 3.0 Å at the minimum, which occurs at ρ ≈ −0.7 Å and which is ≈200 kcal/mol lower than the asymptotic level. For ρ < −0.7 Å, the energy increases again, and r decreases to ~2 Å, so it appears that in this case, O₂ forms a strong bond with Al₄, separated into two single O atoms adsorbed around the pyramid.

A completely similar picture is obtained from the DFT calculations (Figures 2b and 3a, b), which, indeed, give a slight barrier, at ρ ≈ 3 Å, probably due to the very accurate Gaussian basis set used. This prompted us to proceed to a more extensive search of the PES using the DFT method. To investigate the plateau at around ρ ≈ 1 Å and r ≈ 2.7 Å, we computed the energy, E, for a systematic change of the Al₁–O₂ height from ρ = −2 to 5 Å and of the O–O separation from r = 1 to 5 Å, both with steps of 0.1 Å.

Figure 3 displays the DFT potential energy surface E(r, ρ) around the plateau. We observe that as O₂ approaches the pyramid from above, there are, apart from the free O₂ local energy minimum at an O–O distance of r = 1.2 Å for an Al₁–O₂ separation ρ > 3 Å, two local energy minima. At ρ ≈ 3 Å above the Al₁ apex, a first barrier toward O₂ adsorption occurs, although much shallower than the corresponding MRCI barrier (of ~24 kcal/mol, which we believe) at ρ ≈ 3 Å. (In our previous paper,18 the DFT calculation, done with lower quality basis functions, around this area had failed.) After this barrier, there is a slight O–O bond elongation to a length of r = 1.4 Å. At about ρ = 1.5 Å, there is a local energy minimum with an O–O distance of r = 1.6 Å, corresponding to where there is a slight binding of each O atom with the Al cluster apex atom Al₁. We will further investigate this local minimum below. Just below this local minimum, a second, more important, transition occurs, at an O–O distance of 2.1 Å, before the O atoms are finally separated toward adsorption between the surface and the apex Al₁ atom of the Al₄ pyramid.

The dashed line in the contour diagram of Figure 3, indicating the O–O bond opening during the adsorption process, is also shown in Figure 2a and b. The above behavior is consistently reproduced by both employed calculational methods, MRCI and DFT, despite the fact that the DFT remote barrier at ρ ≈ 3 Å is much shallower than that of MRCI (see also Figure 4).

To obtain an idea of the electron redistribution in passing, consecutively, through the above two transitions, we examined the corresponding Kohn–Sham highest occupied molecular orbitals (HOMO), as shown in the next figures.

Figure 4 shows the HOMO orbitals around the first (remote) transition from molecular O₂ toward the intermediate trap. The second row corresponds to the transition (on the examined plane), and the first and third rows correspond to O₂ positions just above and below the remote barrier. The spin-up HOMO (left side of Figure 4) belongs entirely to the Al pyramid, but through the spin-down HOMO (right side of Figure 4), some
electron density is transferred from the Al pyramid to $O_2$, as clearly seen at the first local minimum in Figure 5.

The first row of Figure 5 shows the HOMO orbitals (left panel, spin-up; right panel, spin-down) at the first local minimum on the plane of Figure 3 (close to the actual trap), where $O_2$ is still parallel to one vertex of the triangular basis. The $Al1-O$ bond length is 1.7 Å; the $O-Al1-O$ angle is 65°.

To investigate this trap, we relaxed the two $O$ atoms to optimize their geometry. Indeed, as seen in the two lower rows of Figure 5, they are trapped above the $Al1$ apex, rotated so that one $O$ atom stabilizes on the extension of one of the side vertices, while the other stabilizes above the same vertex. The binding energy (from the free $O_2$) is $\sim 70$ (DFT value) to 80 (MRCI value) kcal/mol. At the trap, there are three kinds of eigen frequencies: two higher (963 and 787 cm$^{-1}$, where the two $O$ atoms vibrate with respect to $Al1$ in phase and out of phase, respectively; the $Al1-O$ bond length changes), three intermediate (340, 309, and 266 cm$^{-1}$, corresponding to $O-Al1-O$ angular oscillations; the $Al1-O$ bond length is unchanged, while the triangular $Al$ basis oscillates slightly, too), and five lower (213, 180, 172, 148, and 51 cm$^{-1}$, where the $AlO_2$ moiety moves with respect to the triangular basis as a whole). In this geometry, there are also two imaginary frequencies at which the triangular basis internally oscillates (linearly and rotationally) with respect to a fixed $AlO_2$ moiety, indicating that this structure is not the ground state of this whole "molecule". Therefore, we checked whether this trap could still exist in a slightly more realistic $Al(111)$ surface environment. We surrounded the triangular basis with 9 more $Al$ atoms (all 12 forming a (111) structure) while keeping the $Al1$ apex above the central triangle, and we relaxed the two $O$ atoms around the trap, thus modelling an adatom at a (111) surface. The trap still exists in such a configuration (Figure 6).

The relevant eigen frequencies in the larger cluster are in the same order of magnitude as in the tetrahedron case, that is, 700–900 cm$^{-1}$ for the $O$ vibrations, 250–350 cm$^{-1}$ for the $O$ rotational oscillations, and 50–200 cm$^{-1}$ for the $AlO_2$ movements. Thus, we believe that if there are apex-$Al$ atoms above the $Al$ (111) surface, the incoming $O_2$ is temporarily trapped (delayed) by them, but the time delay, $\sim 40$ fs, is experimentally rather undetectable. In the trap, the two $O$ atoms are negatively charged by 0.2 $e$ each, (Mulliken population) taken from the triangular basis, and the apex $Al1$ is neutral.

Next, we were not able to find the transition state from this trap toward the lower lying adsorption state, but since there is no essential difference in the orbitals of the actual trap and of the local minimum of Figure 3, (cf. Figure 5a,b vs c,d), we show, indicatively, in Figure 7 the electron density transfer around the second (lower) barrier of Figure 3.

Figure 7 shows the spin-up and spin-down HOMO of the triplet, around the transition barrier (height of $\approx 1.5$ Å), as $O_2$ approaches the top of the $Al1$ pyramid. The second row corresponds to the barrier; the first and third rows correspond to $O_2$ positions just above and below the barrier: The spin-down HOMO changes entirely during the transition; the spin-up HOMO is affected, but eventually it remains unaltered. The barrier from the trap toward the final adsorption state is $\sim 10$ kcal/mol, and the difference between the trap and the final adsorption state is $\sim 115$ (DFT) to 120 (MRCI) kcal/mol.

V. Conclusions

We examined the adsorption of $O_2$ on an apex atom of an $Al4$ tetrahedron of 2.7 Å $Al-Al$ bond length (in the total spin triplet state) by both ab initio MRDCI and DFT methods. Such a configuration might be relevant for the understanding of the interaction of $O_2$ with defect sites on $Al$, such as adatoms. We found, similar to other DFT calculations of $O_2$ interacting with small flat $Al$ clusters using hybrid functional, that the $O_2$ adsorption at the apex of the cluster is hindered by a barrier. This means that an $Al$ adatom is not necessarily more active toward $O_2$ dissociation than $Al$ atoms in a planar geometry. This
also means that the vanishing barrier for the O₂ adsorption on Al(111) found in periodic DFT calculations might still be an artifact of the employed functionals (rather than the basis functions), as indicated by the larger barrier found in MRCI calculations than in DFT calculations.

Using DFT, we mapped out the potential energy surface of the O₂–Al₄ interaction in some more detail. According to these calculations, O₂ can be temporarily trapped to a local energy minimum above the apex while approaching the apex of the pyramid, resulting in as yet experimentally undetectable time delay of about 40 fs before it is finally adsorbed dissociatively below the apex (in a deeper energy minimum): When O₂ approaches the apex Al atom, the elongated O₂ molecule is trapped on top of it with a binding energy (relative to the free O₂) of ∼70–80 kcal/mol before it overcomes a barrier of ∼10 kcal/mol toward full dissociative adsorption below the apex Al atom, ∼115–120 kcal/mol lower than the trap. In the trap, O₂ attracts some electronic charge from the cluster basis Al atoms (≈0.4e in Mulliken population), whereas the intermediate apex Al atom is neutral. Of course, this charge transfer refers to our small cluster with a limited number of electrons and not to a semi-infinite substrate with an infinite reservoir of electrons at the Fermi level.

Acknowledgment. This work was supported in part by the IKYDA program of the German Academic Exchange Service (DAAD) and the Greek State Scholarships Foundation (I.K.Y.). Partial support of this work through the Excellence in the Research Institutes program, supervised by the General Secretariat for Research and Technology/Ministry of Development, Greece (Phase I and II, Projects 64769 and 200501330081) is gratefully acknowledged.

References and Notes


JP1052198