The Reaction Rates of $O_2$ with Closed-Shell and Open-Shell $Al_x^-$ and $Ga_x^-$ Clusters under Single-Collision Conditions: Experimental and Theoretical Investigations toward a Generally Valid Model for the Hindered Reactions of $O_2$ with Metal Atom Clusters

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Supporting Information

ABSTRACT: In order to characterize the oxidation of metallic surfaces, the reactions of $O_2$ with a number of $Al_x^-$ and, for the first time, $Ga_x^-$ clusters as molecular models have been investigated, and the results are presented here for $x = 9 \text{–} 14$. The rate coefficients were determined with FT-ICR mass spectrometry under single-collision conditions at $O_2$ pressures of $\sim 10^{-7}$ mbar. In this way, the qualitatively known differences in the reactivities of the even- and odd-numbered clusters toward $O_2$ could be quantified experimentally. To obtain information about the elementary steps, we additionally performed density functional theory calculations. The results show that for both even- and odd-numbered clusters the formation of the most stable dioxide species, $[M_2O_2]^-$, proceeds via the less stable peroxo species, $[M_x^+\cdot\cdot\cdotO_2]^-$, which contains $M-O-O-M$ moieties. We conclude that the formation of these peroxo intermediates may be a reason for the decreased reactivity of the metal clusters toward $O_2$. This could be one of the main reasons why $O_2$ reactions with metal surfaces proceed more slowly than $Cl_2$ reactions with such surfaces, even though $O_2$ reactions with both $Al$ metal and $Al$ clusters are more exothermic than are reactions of $Cl_2$ with them. Furthermore, our results indicate that the spin-forbidden reactions of $^3$O$_2$ with closed-shell clusters and the spin-allowed reactions with open-shell clusters to give singlet $[M_x^+\cdot\cdot\cdotO_2]^-$ are the root cause for the observed even/odd differences in reactivity.

INTRODUCTION

The hindered reactivity of $O_2$ with metal surfaces, in contrast to their fast reactions with $Cl_2$, is well-known in classical inorganic chemistry and is based on some important differences between these reactants. In the case of a base metal such as $Al$, the $O_2$ reaction is strongly exothermic with respect to the formation of $Al_2O_3$ ($2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3; \Delta H_f^{\ominus} = -1676$ kJ mol$^{-1}$, that is, 838 kJ per 1 mol $Al$), while less energy is gained in the $Cl_2$ reaction, where $AlCl_3$ is formed ($Al + \frac{3}{2}Cl_2 \rightarrow AlCl_3; \Delta H_f^{\ominus} = -705$ kJ mol$^{-1}$).² Because of the high stability of $Al_2O_3$, it remains steadfastly on the surface of the aluminum metal, protecting it and prohibiting further oxidation of the metal. Only at high temperatures (>1200 °C), where $Al_2O_3$ reacts with $Al$ metal to form the low valent oxide molecule $Al-O-Al$, can alumina be vaporized and removed from the metal surface.³ The formation of this linear molecule, $Al-O-Al$, is the essential step in the deterioration of the aluminum surface after reaction of $O_2$ with solid $Al$ and, as we will see, with $Al_x^-$ clusters:

$$Al_x^- + O_2 \rightarrow Al_{x-4}^- + 2Al_2O_3(g) \quad (1a)$$

If an excess of $O_2$ is applied, the $Al_2O_3$ molecules are easily oxidized to solid $Al_2O_3$, and simultaneously a large amount of energy is gained:

$$Al_2O_3(g) + O_2(g) \rightarrow Al_2O_3(s) \quad (1b)$$

with $\Delta_fH^{\ominus} = -1530.5$ kJ mol$^{-1}$.² In contrast, the chlorination of $Al$ runs at even low temperatures (>200 °C), and the reaction proceeds completely to $AlCl_3$ (or to $Al_2Cl_6$), which is a volatile solid compound even at these temperatures. Therefore, this reaction continues until the $Al$ metal is consumed.⁴

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Besides the thermodynamic data and experimental results, which favor a fast and complete reaction of Al metal with Cl2 in comparison to O2, there is a molecular-kinetic reason for the slower reaction of O2 a stepwise transfer of four electrons from Al to O2 via several intermediates containing ALO bonds:

\[ \text{O}_2 \rightarrow \text{O}_2^- \rightarrow \text{O}_2^{2-} \rightarrow \text{O}_2^{3-} \]

(superoxo) (peroxo) (oxide)

In contrast, in the case of Cl2 only one intermediate is possible, which contains two AlCl bonds, because every Cl2 molecule takes two electrons to form two Cl− anions.

The investigation of the complex reaction of O2 molecules with metal atom surfaces was and still is a challenging problem for theory and experiment. On the experimental side, it mainly involved the use of photophysical methods such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM). However, the investigation of surfaces of base metals bears a fundamental difficulty. This is because the 5 eV bond energy (BE) of an Al−O bond (in an Al−O−O−Al fragment) is equivalent to the energy necessary to cleave the O−O bond in the O2 molecule, producing two O atoms (the O2 BE is 5.16 eV). A peroxo intermediate fragment Al−O−O−Al, containing two Al−O bonds, will therefore be highly excited (5 eV excess energy) and thus O atoms can also be ejected from the surface. In order to avoid such difficulties, mainly O2 reactions with surfaces of noble metals have been investigated. There, the M−O bond energy is much smaller (e.g., for Pd−O, 2.87 eV from PdO(g), and for Pt−O, 3.28 eV), and therefore it is possible to detect intermediate fragments, for example, Pt−O−O−Pt, with possible methods.

Besides the investigations of the hindered O2 reactions with metal surfaces by using microscopic methods (AFM, STM), a further experimental approach, namely, mass spectrometric investigations of metal atom clusters and their O2 reactions, promises to give a deeper insight into this complex reaction mechanism.

Al± clusters have been investigated in many experimental and theoretical papers during the last two decades. However, only the Al13− cluster appears to be an ideal molecular model for studying reactions involving bulk metals. The surprising similarity for the chlorination of the Al13− cluster and Al metal illustrates the similar thermodynamic behavior.

\[ \text{Al}_{13}^− + 3\text{Cl}_2 \rightarrow \text{Al}_{11}^− + 2\text{AlCl}_3(g) \]

\[ \Delta_r H = -1137 \text{ kJ mol}^{-1} \quad \text{(calcd)} \]

\[ 2\text{Al}(g) + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3(g) \]

\[ \Delta_r H = -1166 \text{ kJ mol}^{-1} \quad \text{(expt)} \]

However, for the observed hindered reaction of the Al13− cluster with O2, note that also the reaction of O2 with bulk Al is unexpectedly slow, there have been given several different explanations: (1) the outstanding electronic stability of Al13− with its 40 valence electron jellium core, (2) the exceptional geometry in which a central Al atom is surrounded by 12 additional Al atoms, which form an icosaahedron around it, that is, a magic geometry, (3) the outstanding electron affinity (3.6 eV) of Al13 which is as large as that of the atomic chlorine atom, and finally (4) the spin-forbidden reaction of triplet O2 with the singlet Al13− species to give singlet Al12− and 2AlClO.(18−21)

It was demonstrated that isolated Al13− ions in an O2 atmosphere of about 10−8 mbar in an ion cyclotron resonance (ICR) trap do not form Al1− species even after about 600 s. In order to show that this hindered Al13− + O2 reaction is not just a special case but is of general interest, we measured the rate coefficients of O2 reactions with a number of Alx clusters near the Al13− species with closed- and open-shell structure. We found slow reactions for Alx, Al11−, and Al13− and comparatively fast reactions for Alx, Al10−, Al12−, and Al14−. The doublet character of the last four species eliminates hindrances caused by the collisional energy. The experimental findings and the analysis of these complex results are the subject of a further publication.

To further study the general importance of the O2 + metal reaction, we have extended our investigation to a number of Ga1− clusters. Though Ga is a homologue of Al, it exhibits many differences: Unexpectedly, the electronegativity (EN) of Ga, at 1.8, is higher than that of Al (1.5). Ga has seven crystalline modifications; these vary in their bond formation from covalent bonding as in the case of boron toward metallic bonding as in a real metal. The α-Ga modification, with one short Ga−Ga bond, often is called a molecular metal, a property that is also reflected in its low melting point of 28 °C. Also, true metal structures like Ga(IV) are observed under high pressure. However, the electronic behavior of naked Ga1− should be similar to that of Al1− clusters since the same number of valence electrons are involved in bonding, for example 40 in the jellium-like Ga13− cluster. Therefore, while reactions of O2 with Ga1− clusters should be electronically similar to reactions with Al1− clusters, they are different from a thermodynamic point of view, because the Ga−O bond energy is considerably smaller than that of Al−O. The Al−O bond strength is much larger, however, than that of all noble metal−oxygen bonds, as the following comparison shows: Al−O = 5.35 eV (from Al2O), Ga−O = 4.59 eV (from Ga2O), and Pd−O = 2.87 eV (from Pd−O2(g)). Accordingly, the mass spectrometric results for the Ga1− clusters presented here can be expected to show whether the model for the Alx− + O2 reactions is valid for other metals that exhibit different thermodynamic properties. The different thermodynamic properties of Ga compounds in comparison to Al compounds are also reflected in procedures for forming Ga1− and Alx clusters. While Alx clusters were formed by laser desorption of solid LiAlH4 Ga1− species can be obtained after laser irradiation of solid GaN, which will be described here for the first time.

The rate coefficients presented in this work were determined by bringing either single-sized clusters or a collection of clusters with different sizes into reaction with O2 under (nearly) single-collision conditions (10−8 mbar). This means that the reaction products are generally detected before a second collision with O2 occurs. This approach is essential in order to study the single elementary steps of the reaction. In contrast, in recent flow tube experiments by other authors at about 0.5 mbar, up to 100 collisions between O2 and a single cluster occur before the products are detected. In these experiments, rate coefficients of O2 with a large number (ca. 50) of Al1− clusters of different size.
were estimated via a data analysis based on a Monte Carlo model.\textsuperscript{20,21}

A comparison of measured rate coefficients with predictions from kinetic theories would allow further conclusions regarding the underlying reaction mechanisms. However, the calculation of rate coefficients from first principles with molecular and transition state data from quantum chemical methods requires a reliable knowledge of barrier heights. For the reactions of \( ^3\text{O}_2 \) with closed- and open-shell \( \text{Al}^- \) and \( \text{Ga}^- \) clusters, these calculations are complicated not only by failure of single-determinant methods but also by the existence of multiple isomeric intermediates.\textsuperscript{27}

On the basis of our experimental results and supported by DFT calculations, we obtained evidence for a model in which the peroxo intermediate \([\text{M}_x\cdots\text{O}_2]^-\), as the earliest species along the reaction coordinate that exhibits a typical arrangement of valence electrons, plays an essential role. This peroxo intermediate is also the prominent species in a more general, hypothetical reaction scheme that is, a Gedanken experiment, which should allow predictions to be made for \( \text{O}_2 \) reaction rates of any metal atom clusters. Within this broader scheme, the oxidation of the \( \text{M}_x^- \) cluster to a \( \text{M}_x^+ \) species with simultaneous reduction of \( \text{O}_2 \) to the \( \text{O}_2^{2-} \) peroxo moiety plays the major role.\textsuperscript{28,1}

\section*{RESULTS AND DISCUSSION}

\textbf{Mechanisms and Rate Coefficients}. Prior to the determination of rate coefficients, we studied qualitatively the reaction pattern of all \( \text{M}_{m/n}^- \) clusters (\( m = \) even-numbered; \( n = \) odd-numbered; \( M = \text{Al}, \text{Ga} \)) with \( \text{O}_2 \). The clusters were first isolated and brought to collision with oxygen at a pressure of about \( 4 \times 10^{-8} \) mbar for several seconds. Let us consider \( \text{Ga}_{m/n}^- \) cluster anions first. For these even-numbered clusters (\( \text{Ga}_{10}^- \), \( \text{Ga}_{12}^- \), \( \text{Ga}_{14}^- \), \( \text{Ga}_{16}^- \), \( \text{Ga}_{18}^- \), \( \text{Ga}_{20}^- \), \( \text{Ga}_{22}^- \), \( \text{Ga}_{24}^- \)), the following spontaneous reactions were observed.\textsuperscript{29}

\begin{align*}
\text{Ga}_{10}^- + \text{O}_2 & \rightarrow \text{Ga}_6^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{10}^- + \text{O}_2 & \rightarrow \text{Ga}_5^- + \text{Ga}_2\text{O} + \text{Ga}_3\text{O} \\
\text{Ga}_{12}^- + \text{O}_2 & \rightarrow \text{Ga}_7^- + \text{Ga}_2\text{O} + \text{Ga}_3\text{O} \\
\text{Ga}_{14}^- + \text{O}_2 & \rightarrow \text{Ga}_{10}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{16}^- + \text{O}_2 & \rightarrow \text{Ga}_{12}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{16}^- + \text{O}_2 & \rightarrow \text{Ga}_{11}^- + \text{Ga}_2\text{O} + \text{Ga}_3\text{O} \\
\text{Ga}_{18}^- + \text{O}_2 & \rightarrow \text{Ga}_{13}^- + \text{Ga}_2\text{O} + \text{Ga}_4\text{O} \\
\text{Ga}_{20}^- + \text{O}_2 & \rightarrow \text{Ga}_{16}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{20}^- + \text{O}_2 & \rightarrow \text{Ga}_{15}^- + \text{Ga}_2\text{O} + \text{Ga}_4\text{O} \\
\text{Ga}_{22}^- + \text{O}_2 & \rightarrow \text{Ga}_{18}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{24}^- + \text{O}_2 & \rightarrow \text{Ga}_{20}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{26}^- + \text{O}_2 & \rightarrow \text{Ga}_{22}^- + 2\text{Ga}_2\text{O} \\
\text{Ga}_{28}^- + \text{O}_2 & \rightarrow \text{Ga}_{24}^- + 2\text{Ga}_2\text{O}
\end{align*}

In contrast to all these spontaneous reactions, the odd-numbered, closed-shell \( \text{Ga}_{m/n}^- \) clusters react at least one order of magnitude more slowly with \( \text{O}_2 \), and only upper limits to the rate coefficients can be given.\textsuperscript{30}

For the corresponding \( \text{Al}_{m/n}^- \) clusters, qualitatively the analogous reactions were observed that is, spontaneous reactions for even-numbered \( \text{Al}_{m/n}^- \) clusters with formation of \( \text{Al}_{m-4}^- \) or \( \text{Al}_{m-5}^- \) fragments. Odd-numbered \( \text{Al}_{m/n}^- \) clusters were found to be much less reactive, \( \text{Al}_{13}^- \) and \( \text{Al}_{25}^- \) being nearly stable in agreement with our former observations\textsuperscript{18} and those of Castleman et al.\textsuperscript{21}

For the determination of rate coefficients, \( \text{O}_2 \) was admitted to the ICR cell by a manual leak valve (Varian) allowing us to maintain a constant partial pressure of \( 3 \times 10^{-10} \) to \( 4 \times 10^{-8} \) mbar in the cell. Note that with this method the maximum pressure was limited to \( \sim 4 \times 10^{-8} \) mbar, because ion detection took place while the reaction gas (\( \text{O}_2 \)) was present in the ICR cell. Rate coefficients for all \( \text{Ga}_{m/n}^- \) clusters are shown in Figure 1.

![Figure 1. Measured rate coefficients for reactions of \( \text{Ga}_{m/n}^- \) clusters with \( \text{O}_2 \). Error bars originate from at least two independent measurements carried out on different days. For numerical values of \( \text{Ga}_9^- \), see Table 2.](image-url)

By knowing the reaction behavior of some single-sized clusters \( \text{M}_x^- \) (see above), we were also able to study and characterize the reactivity of a whole collection of differently sized clusters (e.g., \( \text{Ga}_{11}^- \), \( \text{Ga}_{22}^- \)) at once and to numerically fit the integrated rate equations of the consecutive reaction steps to the experimental data to obtain pseudo-first-order rate coefficients, \( k_i \) (see Supporting Information). For these calculations, the software \textit{DetMecha}\textsuperscript{31} was used.

Since for several cluster types the rate coefficient \( k_i \) was determined by isolating the single clusters first (e.g., \( \text{Ga}_{10}^- \), \( \text{Ga}_{13}^- \), \( \text{Ga}_{22}^- \), and \( \text{Al}_{13}^- \)), the reliability of the collective measurements has been confirmed because values from both measurements agree well.

In order to derive reliable reaction rates of the \( \text{M}_{m/n}^- \) clusters, all ion intensities were normalized to the intensity of \( \text{Ga}_{9}^- \). This is justified because (1) the rate coefficient of \( \text{M}_9^- \) with \( \text{O}_2 \) is much smaller (about a factor of 100) compared with the other (even-numbered) clusters and (2) there is no cluster that reacts to give \( \text{M}_9^- \) because for \( \text{Al}_{13}^- \) and \( \text{Ga}_{13}^- \), even at prolonged reaction times of up to 600 s, no reaction with \( \text{O}_2 \) was observed (cf. above).

In order to generate \( \text{Al}_{m/n}^- \) clusters, the \( \text{Al}_{m/n}^- \) clusters were exposed to a hydrogen atmosphere at \( 10^{-2} \) mbar for 1–3 s.\textsuperscript{18}

\textbf{Model for the Primary, Rate-Determining Step}. The overall reactions of \( \text{Al}_n^- \) and \( \text{Ga}_n^- \) clusters with \( \text{O}_2 \) are exemplarily summarized for \( \text{Al}_n^- \) clusters in the following equations, which are divided into spin-forbidden (2a) and spin-allowed reactions (2b):

\begin{align*}
\text{even-numbered clusters} \\
1\text{Al}_n^- + 3\text{O}_2 & \rightarrow 1\text{Al}_{n-4}^- + 2\text{Al}_2\text{O} \quad (2a) \\
& \rightarrow 2\text{Al}_2\text{O} \\
\end{align*}
Figure 2. (left) Schematic presentation of the reaction path of an Al\textsubscript{13}\textsuperscript{−} cluster with \textsuperscript{3}O\textsubscript{2}. As a spin-forbidden example, the hindered reaction of the Al\textsubscript{13}\textsuperscript{−} cluster is shown: Al\textsubscript{13}\textsuperscript{−} reacts via spin transition to the peroxy-bonded O\textsubscript{2}\textsuperscript{−} intermediate X (|Al\textsubscript{13}\textsuperscript{−} + O\textsubscript{2} → |Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−} X\textsuperscript{−}]) (energy gain Δ\textit{E}X) and finally to the more stable anion F, |Al\textsubscript{13}\textsuperscript{−}O\textsubscript{2}\textsuperscript{−} X\textsuperscript{−}] (energy gain Δ\textit{E}F) corresponding to complete oxidation of the Al\textsubscript{13}\textsuperscript{−} cluster with a single O\textsubscript{2} molecule (cf. text). (right) Spontaneous reaction of Al\textsubscript{13}\textsuperscript{−} cluster with Cl\textsubscript{2} to the completely oxidized [Al\textsubscript{13}Cl\textsubscript{2}]	extsuperscript{3+} intermediate, which rapidly decomposes to Al\textsubscript{11} + 2AlCl\textsubscript{3}.

Table 1. Calculated (DFT) Values of Δ\textit{E}X and Δ\textit{E}X + Δ\textit{E}F (eV) for the Energy Gain from the Reactants (e.g., Ga\textsubscript{13}\textsuperscript{−} + \textsuperscript{3}O\textsubscript{2}) to the Side-on Bonded Intermediate X (e.g., [Ga\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−} X\textsuperscript{−}] ) and to the Ground State F (e.g., [Ga\textsubscript{13}O\textsubscript{2}])\textsuperscript{a}

<table>
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<th></th>
<th>Ga\textsubscript{9}</th>
<th>Ga\textsubscript{10}</th>
<th>Ga\textsubscript{11}</th>
<th>Ga\textsubscript{12}</th>
<th>Ga\textsubscript{13}</th>
<th>Al\textsubscript{11}</th>
<th>Al\textsubscript{14}</th>
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<td>1.92</td>
<td>1.87</td>
<td>1.83</td>
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<td>−Δ\textit{E}X + −Δ\textit{E}F</td>
<td>4.58</td>
<td>5.45</td>
<td>4.62</td>
<td>4.73</td>
<td>4.64</td>
<td>5.12</td>
<td>6.99</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For explanation, see Figure 2.

even-numbered clusters

\[ 2\text{Al}_{n}^{−} + \text{O}_{2} \rightarrow \text{Al}_{n−4}^{−} + 2\text{Al}_{2}\text{O} \quad (2b) \]

Note, however, that this four electron reaction\textsuperscript{32} is only the simple summarization of a very complex reaction route in which many intermediates are involved. Since quantum chemical calculations of the complex potential energy surface (PES) for the \textit{Al}_{n}^{−} + \text{O}_{2} reactions are not expected to give reliable results for transition states, we tried to develop a plausible model by correlating our measured rate coefficients with the potential energies of stable and metastable species. Additional information is gained from the different reaction rates of \textit{Al}_{n}^{−} clusters with Cl\textsubscript{2} and with O\textsubscript{2} if no spin transition occurs. From our DFT calculations, it follows that the first well-defined intermediate in every Al\textsubscript{13}\textsuperscript{−} + O\textsubscript{2} reaction is a [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] species (in the following denoted by X) in which a peroxy (O\textsubscript{2}\textsuperscript{−}) group is polar-bonded to the \textit{Al}_{13}\textsuperscript{−} cluster via two oxidized Al atoms (Al\textsuperscript{3+}). In Figure 2, the situation is exemplified for Al\textsubscript{13}\textsuperscript{−} + O\textsubscript{2} with [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] as the intermediate X. Note that in the following, the stabilization energy of X with respect to the reactants is denoted by Δ\textit{E}X. For all even-numbered Al\textsubscript{13−m} clusters, this intermediate X is in a doublet state and formed without spin restrictions; for the odd-numbered clusters Al\textsubscript{m}−, however, X is in a singlet state, and a spin flip is necessary.

The peroxy moiety O\textsubscript{2}\textsuperscript{−} within these intermediates (also present in H\textsubscript{2}O\textsubscript{2}, for example),\textsuperscript{1} bonded to two different metal atoms of the cluster, represents a chemically well-known situation with classical bonding,\textsuperscript{28} which is isoelectronic to that of the \textit{F}X molecule. Therefore, an intermediate X of this type can be expected to have a pronounced local minimum on the PES in accordance with our DFT results.

Thus, the [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] intermediate X with its local energy minimum Δ\textit{E}X (Table 1) corresponds to the first well-defined step along the reaction route, where the O\textsubscript{2} molecule has obtained two electrons from the Al\textsubscript{13}\textsuperscript{−} cluster. The [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] intermediate has O\textsubscript{2} bonded side-on, bridging between two aluminum atoms. With the transfer of two electrons, the Al\textsubscript{13}\textsuperscript{−} cluster is oxidized to an Al\textsubscript{11} Cl\textsubscript{2}, and the O−O bond distance is elongated becoming an O−O single bond in the O\textsubscript{2}\textsuperscript{−} moieties, the normal octet of electrons is maintained on each oxygen atom. This [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] intermediate reflects just the first step of the complete reaction with a four-electron transfer to two bridging O\textsuperscript{−} ions of the final [Al\textsubscript{11}Cl\textsubscript{2}][Al\textsubscript{2}...2O\textsubscript{2}\textsuperscript{−}] dioxide cluster F (Figure 2), which represents the global minimum.

Under high-vacuum conditions, collisional stabilization of the vibrationally excited dioxide [Al\textsubscript{13}Cl\textsubscript{2}]	extsuperscript{−} cluster F (see Table 1) can be neglected because a low-lying decomposition channel giving Al\textsubscript{11}Cl\textsubscript{2} + 2AlCl\textsubscript{3} exists (Figure 3).\textsuperscript{34} As illustrated in Figure 2 and discussed in the following, it is probably not the formation of this final, highly vibrationally excited dioxide cluster F, (Δ\textit{E}X + Δ\textit{E}F), that determines the overall rate constant but instead, the formation of the above-mentioned peroxy-bonded [Al\textsubscript{13}\textsuperscript{−}...O\textsubscript{2}\textsuperscript{−}] intermediate X (Figure 2) with a much lower energy gain Δ\textit{E}X in the range of 2–3 eV. The calculated energies of the ground state F and the intermediate X of all Al\textsubscript{13}\textsuperscript{−m} and Ga\textsubscript{13}\textsuperscript{−m} clusters under discussion are listed in Table 1, and the corresponding structures are presented in the Supporting Information.

This conclusion is supported by our previous investigations on (spin-allowed) reactions of Al\textsubscript{13}\textsuperscript{−} with Cl\textsubscript{2}, in which Al\textsubscript{11}− and 2AlCl\textsubscript{3} molecules are formed spontaneously via decomposition of the excited [Al\textsubscript{13}Cl\textsubscript{2}]	extsuperscript{−} cluster and which are faster (3–6 times)\textsuperscript{6,33} than those of the even-numbered Al\textsubscript{13}\textsuperscript{−m}/Ga\textsubscript{13}\textsuperscript{−m} clusters with O\textsubscript{2}, which are also spin-allowed.

Despite the smaller energy gain in forming the most stable oxidized cluster (4.5 eV for Al\textsubscript{13}− + Cl\textsubscript{2} \rightarrow [Al\textsubscript{13}\textsubscript{−}...O\textsubscript{2}\textsuperscript{−}] compared with 7 eV for Al\textsubscript{13}− + O\textsubscript{2} \rightarrow [Al\textsubscript{13}\textsubscript{−}...O\textsubscript{2}\textsuperscript{−}]), the overall reaction Al\textsubscript{13}− + Cl\textsubscript{2} is faster than the overall reaction Al\textsubscript{13}− + O\textsubscript{2}. From this observation, we conclude that for the Al\textsubscript{13}\textsuperscript{−} + O\textsubscript{2} reactions, a less excited intermediate is likely to exist that determines the rate
of the overall reaction. From our quantum chemical calculations, it follows that this intermediate is the peroxo species, X, \([\text{Al}_{m/0} \cdots \text{O}_2^{2-}]^{-}\).

On the basis of these arguments, we propose the following general model for the Al\(_{m/0}^{-}\) + \(\text{O}_2\) reaction: The energy gain \(\Delta E^X\) for the formation of the peroxo intermediate determines the overall rate of reaction. The larger the energy gain, the larger the rate coefficient. This could be a manifestation of the Evans–Polanyi principle (see e.g., ref 35). If the reaction is spin-forbidden, the rate is slowed down.

**The High Reactivity of the Even-Numbered Al\(_m^-\) and Ga\(_m^-\) Clusters.** In order to verify the above-mentioned model, we examined first the open-shell gallium clusters Ga\(_{10}^-\), Ga\(_{12}^-\), and Ga\(_{14}^-\), for which the rate coefficients can be determined more accurately than for the similar Al\(_{10}^-\), Al\(_{12}^-\), and Al\(_{14}^-\) clusters. This is because the intensities and particle densities of the Ga\(_{m/0}^-\) clusters are higher than those for the Al\(_{m/0}^-\) clusters due to their different formation process. In any case, the reactions of even-numbered Al\(_m^-\) and Ga\(_m^-\) clusters with \(\text{O}_2\) are spin-forbidden (cf. eq 2b) and therefore can proceed spontaneously, which is confirmed by our experiments. The experimentally determined rate coefficients are displayed in Figure 1 and collected in Table 2.

The rate coefficients increase in the sequence, Ga\(_{12}^-\) ≈ Ga\(_{16}^-\) < Ga\(_{10}^-\) < Ga\(_{14}^-\). Even accounting for absolute errors, the measured rate coefficients are below the Langevin limit by a factor of 20, this limit being on the order of \(5 \times 10^{-10}\) cm\(^3\) s\(^{-1}\) for the Ga\(_{m/0}^-\) + \(\text{O}_2\) reactions (polarizability of \(\text{O}_2 = 1.58 \times 10^{-30}\) cm\(^3\)).

Clearly, the rate coefficients increase in the sequence, Ga\(_{12}^-\) ≈ Ga\(_{16}^-\) < Ga\(_{10}^-\) < Ga\(_{14}^-\). Even accounting for absolute errors, the measured rate coefficients are below the Langevin limit by a factor of 20, this limit being on the order of \(5 \times 10^{-10}\) cm\(^3\) s\(^{-1}\) for the Ga\(_{m/0}^-\) + \(\text{O}_2\) reactions (polarizability of \(\text{O}_2 = 1.58 \times 10^{-30}\) cm\(^3\)).

Table 2. Experimentally Determined Rate Coefficients [10\(^{-11}\) cm\(^3\) s\(^{-1}\)]

<table>
<thead>
<tr>
<th>Cluster</th>
<th>(G_{2a}^-)</th>
<th>(G_{2b}^{-})</th>
<th>(G_{3a}^{-})</th>
<th>(G_{3b}^{-})</th>
<th>(G_{4a}^{-})</th>
<th>(G_{4b}^{-})</th>
<th>(G_{5a}^{-})</th>
<th>(G_{5b}^{-})</th>
<th>(G_{6a}^{-})</th>
<th>(G_{6b}^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_{13}^-)</td>
<td>0.03(^b)</td>
<td>2.5 ± 0.1</td>
<td>2.0 ± 0.3</td>
<td>0.01(^b)</td>
<td>4.5 ± 0.4</td>
<td>0.04(^b)</td>
<td>1.9 ± 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Al}_{15}^-)</td>
<td>8.8 ± 3.9</td>
<td>6.0 ± 0.6</td>
<td>3.0 ± 0.3</td>
<td>4.5 ± 0.6</td>
<td>4.2 ± 0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The given error is derived from at least two independent measurements. Note that the absolute error is estimated to be on the order of ±50% and is mainly due to uncertainties of the pressure measurement. \(^b\)Only the upper limit could be determined.
reaction rates (see preceding); that is, the Ga$_{14}^-$ cluster exhibits the highest reactivity of all even-numbered Ga$_n^-$ clusters because of its high exoergicity for the formation of the rate-determining peroxo intermediate, X, for example, 2.1 eV for [Ga$_{14}^-$⋅O$_2^-_2$].

This interpretation is surprisingly supported by kinetic investigations of the O$_2$ reactions with alkyl radicals, a completely different reaction system. As can be seen from Table 3, for both reactions (with open-shell Ga$_n^-$ clusters and alkyl radicals), not only are the absolute rate coefficients very similar, but also a correlation is seen between the rate coefficients and the exoergicity of the association step.

The Low Reactivity of Odd-Numbered Al$_n^-$ and Ga$_n^-$ Clusters. The fast O$_2$ reactions of all even-numbered Ga$_n^-$ clusters are in contrast to the hindered reactions of the odd-numbered Ga$_n^-$ clusters with rate coefficients below the Langevin limit by a factor of >1000 (cf. Figure 1 and Table 2). Like in the case of the Al$_{13}^-$ and Ga$_{13}^-$ clusters, an energy barrier has to be overcome during which the spin transition proceeds. This barrier, as with the even-numbered Ga$_n^-$ clusters, should depend also on the stability of the peroxo intermediate X, for example, [M$_{14}^-_2$⋅O$_2^-_2$]. For the Ga$_{13}^-$ cluster, the energy gain for this side-on intermediate is −1.14 eV. Furthermore, also for adjacent odd-numbered Ga$_n^-$ clusters, the relationship between $\Delta E^X$ and the rate coefficient can be expected to apply. For Ga$_9^-$ and Ga$_{11}^-$, the following $\Delta E^X$ values are calculated: −1.84 and −1.87 eV (Table 2). From these more exoergic reactions, in comparison to Ga$_{13}^-$ (−1.14 eV), a faster reaction than for Ga$_{13}^-$ should be expected. But unfortunately, for each of these three clusters, the rate coefficient is too small to be measured exactly under our experimental conditions; that is, only an upper limit can be given. Moreover, since the situation for the O$_2$ reaction with Ga$_{13}^-$ is unexpectedly complex (see Supporting Information), one should only compare Ga$_9^-$ and Ga$_{11}^-$. Specifically, Ga$_{13}^-$ exhibits the smallest and Ga$_{11^-}$ the largest upper limit, which is at least in line with our proposed correlation.

Comparison of Even- and Odd-Numbered Clusters. So far it seems as if a consistent picture can be drawn within the series of odd- and even-numbered Al$_n^-$ and Ga$_n^-$ clusters in the limited size windows, Ga$_9^-$ to Ga$_{14}^-$ and Al$_{13}^-$ to Al$_{14}^-$. Furthermore, this picture is also valid, if one compares the slowest and the fastest reaction of an even/odd cluster pair. The $\Delta E^X$ values for the formation of the peroxo intermediates X of Al$_{13}^-$ and Al$_{14}^-_2$ are −2.2 and −3.1 eV, respectively. For the analogous Ga$_{13}^-_2$ and Ga$_{14}^-$ pair, the following $\Delta E^X$ values are calculated: −1.14 and −2.1 eV, respectively. In the case of the Ga clusters, an increase of a factor of ∼400 is observed for the rate coefficients (Table 2).

The moderate correlation between the $\Delta E^X$ values and the rate coefficients for the M$_{13}^-$/M$_{14}^-$ pair gives a first indication that there must be an additional influence, besides energy, on the reaction rate. This assumption is confirmed by the following example, for which drastically different reaction rates are observed even though the $\Delta E^X$ values are similar. As shown above, there are fast spontaneous reactions for Ga$_{10}^-$ and Ga$_{12}^-$ with $\Delta E^X$ values of −1.92 and −1.83 eV, respectively. Though the $\Delta E^X$ values for Ga$_9^-$ and Ga$_{11}^-_2$ (−1.84 and −1.87 eV, respectively) are in the same range, the rate coefficients for the latter ones are about 100 times slower (see Table 2).

Obviously, there is a rate-decreasing process for the odd-numbered Ga$_n^-$ clusters, because an accelerating process for the even-numbered Ga$_n^-$ clusters can be ruled out.

The spin-forbidden transition during the slow reaction of the odd-numbered clusters (e.g., singlet Al$_{13}^-$ with O$_2$ to the singlet [Al$_{13}^-_2$⋅O$_2^-_2$] intermediate) should cause an additional increase of the barrier, which in a first approximation was discussed above, as being based only on the relatively low exoergicity $\Delta E^X$ of the reaction.

Therefore, the striking difference between the rate coefficients for the even- and odd-numbered clusters gives a strong indication that the hindered O$_2$ reaction with closed-shell clusters is based on an additional barrier caused by the spin transition.

Can Reactivities for Size-Similar Open- And Closed-Shell Clusters Be Estimated? Besides the special effect of the spin transition, which causes a dramatic decrease of the reaction rate, there is clearly a significant correlation between the Al$_{13}^-$/Ga$_{13}^-$ + O$_2$ reaction rates of different clusters and the energy gain $\Delta E^X$ from the educts to the peroxo intermediates, which have been calculated with DFT methods. Now the question arises whether it is possible to make a simpler prediction about the reactivity of such clusters based on the $\Delta E^X$ correlation.

In order to illustrate this approach, we have developed a thermodynamic cycle leading to the peroxo intermediate X, which is shown in Figure 3. Using the Al$_{13}^-$ cluster as a prominent example, the cycle involves the reactants $^1$Al$_{13}^-$ and $^3$O$_2$, which react with a $\Delta E^X$ value of −2.21 eV (Table 2) to form X, [$^1$Al$_{13}^-_2$⋅O$_2^-_2$].

This model process begins with the two-step oxidation (EA + IE) of Al$_{13}^-$ to Al$_{13}^-$ (A) and the two-step reduction of O$_2$ to the singlet dianion O$_2^-_2$ (B) (isoelectronic to the F$_2$ molecule). Subsequently, the Coulomb attraction between Al$_{13}^-$ and O$_2^-_2$ and the formation of two Al−O bonds via charge neutralization proceed, releasing energy, and finally the [$^3$Al$_{13}^-_2$⋅O$_2^-_2$] intermediate, X, is formed (C). Since during this whole process step C is nearly the same for Al$_{13}^-$ and Ga$_{13}^-$, provided they are of similar size as those discussed in this paper (e.g., Ga$_9^-$, Ga$_{11}^-$, and Ga$_{13}^-$ or Ga$_{10}^-$, Ga$_{12}^-$, and Ga$_{14}^-$), the energy gain $\Delta E^X$ calculated with DFT methods should be mainly reflected by the differences in step A. The energy values of step A for some Al$_{13}^-$/Ga$_{13}^-$ clusters have been calculated and are collected in Table 4. These values mainly determine the $\Delta E^X$ values and therefore the rate coefficients (Figure 3): The smaller the value of $E(A) = EA + IE$, the more negative the value of $\Delta E^X$, as the exoergic formation of Ga−O/Al−O bonds, step C, will further exceed A.

In the following, we will concentrate on the Ga$_n^-$ cluster reactions. First we look at the spontaneous reactions of Ga$_{10}^-$, Ga$_{12}^-$, and Ga$_{14}^-$, and then the reaction with Ga$_{14}^-$ exhibits the largest rate coefficient. This property of Ga$_{14}^-$ is in line with its smallest value of $E(A)$ (8.57 eV), while for the slower reaction of Ga$_{12}^-$, the largest value of $E(A)$ (8.87 eV) has been obtained. Therefore, as mentioned above, the values of $E(A)$ for the clusters Ga$_{10}^-$, Ga$_{12}^-$, and Ga$_{14}^-$ are in line with the observed increasing reactivity toward O$_2$ of these Ga$_n^-$ clusters: Ga$_{12}^- < Ga_{10}^- < Ga_{14}^-$.
This simple ionic model is also in line with the reactivity of the closed-shell clusters Ga_9^-, Ga_11^-, and Ga_13^-.

Consequences from the Predicted Reactivity Based on the Ionic Model: Spin Transition Causes an Additional Hindrance. What about the validity of this simple model if one compares even- and odd-numbered Al_n^-/Ga_n^- clusters? The difference, \( \Delta E(A) \), of the E(A) values (Figure 3, Table 4) for Ga_13^- and Ga_14^- (\( \Delta E(A) = 9.39 \pm 8.57 \text{ eV} = 0.82 \text{ eV} \)) corresponds to a strong increase in the O_2 reactivity from Ga_13^- to Ga_14^- by over three orders of magnitude. The acceleration of the reaction is less prominent from Ga_11^- to Ga_13^- (\( \Delta E(A) = 0.3 \text{ eV} \)) and the smallest difference is to be expected for the pair Ga_9^- to Ga_10^- (\( \Delta E(A) = 0.1 \text{ eV} \)). However, since even the low value of \( \Delta E(A) = 0.1 \text{ eV} \) is contrasted by an observed increase in the O_2 reactivity from Ga_9^- to Ga_10^- of about two orders of magnitude, there must be an additional factor that will be responsible for this large difference in the reaction rates. Furthermore, even the large \( \Delta E(A) \) value between Ga_13^- and Ga_14^- may be not sufficient to explain the strongly different reaction rates between the slowest (Ga_13^-) and the fastest (Ga_14^-) reacting cluster alone. Consequently, there has to be a further factor that decreases the reaction rate of the odd clusters (Ga_11^-, Ga_13^-, Ga_15^-) so drastically. This contestion, as discussed above, can only be the hindered spin transition, which, for example, makes the Ga_13^- + O_2 reaction as well as the Al_13 + O_2 reaction extremely slow.

The Reactivity of Al_{13}H^- and Al_{14}H^- Clusters. All in all, our proposed model seems to be on solid ground. Nevertheless, we expand our discussion to two hydrogen-containing Al clusters, which already had given strong experimental indications of the essential influence of the spin conservation rule.\(^{18,20}\) If one H atom is added, then also one electron is added to the cluster, and consequently, the O_2 reactivity changes dramatically. The Al_{13}H^- species as an open-shell cluster is highly reactive in contrast to the inert Al_{13}^- cluster, and the Al_{14}H^- closed-shell cluster is strongly unreactive in contrast to the fast reaction of Al_{14}^-.

We have roughly verified this change, which has been shown experimentally for Al_{13}H^- and Al_{14}H^-\(^{18}\), by DFT calculations. A detailed discussion would require a separate paper, since many isomers have to be included for these Al_{13}H^- clusters in which the H atom can easily migrate on the cluster surface.\(^{43}\) Therefore, only a small number of isomers (\( \text{Al}_{13}H^-(/\text{Al}_{13}H^-O_2^-/\text{Al}_{13}H^-O_2^-)^-/\text{Al}_{13}H^-/\text{Al}_{13}H^-O_2^-/\text{Al}_{13}H^-O_2^-)^- \)) were considered in our calculations. As was the case in the hydrogen-free clusters, energy gains were seen when going from reactants to the intermediate X and again going from X to the final product F. Some results are listed in the Supporting Information, from which the following conclusion can be drawn: The \( \Delta E^x \) and the \( \Delta E^f \) values are similar to those of the H-free clusters Al_{13}^- and Al_{14}^-.

**CONCLUSION AND OUTLOOK**

In order to understand the slower reactions of Al_n^- clusters with O_2 compared with their fast reactions with Cl_2, we have investigated a number of spin-allowed and spin-forbidden O_2 reactions with Al_n^- clusters in the size neighborhood of the Al_{13}^- cluster. Furthermore, we have extended our investigations to similar Ga_n^- clusters to examine whether our results are restricted to Al or are also valid for other metal atom clusters, as well as for the oxidation of metal surfaces in general. Accordingly, rate coefficients of the reactions of O_2 with Al_n^- and Ga_n^- (\( n = 9-14 \)) near the size of the exceptional M_{13}^- have been measured by FTICR mass spectrometry under single collision conditions, that is, subsequent fast unimolecular reactions proceed before the next collision occurs. These measurements, which quantify the even/odd properties of these clusters, in particular, the fast reaction of the even-numbered, open-shell clusters and the slow, spin-forbidden reactions of the odd-numbered, closed-shell clusters, have been complemented by DFT calculations in which we have computed the ground state energies of the reactants, the intermediates, and the products. These results provide guidelines for the discussion of the experimentally determined rate coefficients. The critical intermediate that determines the reaction rate has a normal valence bonding character, because it contains the well-known peroxo unit (O-O)^2-, which is bonded to two neighboring metal atoms on the surface of the M_n^- cluster, after it is partially oxidized to a M^+ cluster. Simultaneously, the O_2 molecule is reduced to the O_2^- moiety. The energy gain, \( \Delta E^x \), during formation of this [M_n^+O-O_2^-] intermediate is correlated to the rate coefficient of the M_n^- + O_2 reaction. The larger \( \Delta E^x \), the larger is the rate coefficient observed (for the spin-allowed reactions). This fundamental conclusion is furthermore supported by (a) the faster O_2 reactions of the Al_n^- clusters in comparison to the Ga_n^- clusters, because the formation of Al-O bonds is more exothermic than the formation of Ga-O bonds, and (b) the spin-allowed reaction of Al_{13}^- clusters with Cl_2 being faster than the spin-forbidden reactions with O_2. This result is in line with our model if in reactions with chlorine, the formation of the highly excited dichloride cluster Al_{13}Cl_2^- is the rate-determining step (e.g., Al_{13}Cl_2^- is excited with 4.5 eV and reacts to give Al_{13}^- + 2 Cl_2) and if in reactions with oxygen the intermediate X (e.g., [Al_{14}^-\cdots-O_2^-]^- with 3.1 eV) represents the critical, rate-determining species.

However, the energy of this intermediate [M_n^+\cdots-O_2^-]^- cannot, by itself, completely account for the experimental findings regarding the reactivity of similar even- and odd-numbered...
clusters (e.g., Ga_{13}^- and Ga_{14}^-). The spin transition during the reaction of the odd-numbered cluster causes an additional hindrance for the $^{3}$O$_2$ reaction. This conclusion has been convincingly confirmed in calculations related to the recent experimental results for the H-containing clusters Al$_{14}$H$^+$ and Al$_{14}$H$. Though the $\Delta E^f$ values of the O$_2$ reactions with Al$_{13}$H$^+$ and Al$_{14}$H$^-$ as well as with Al$_{14}$H$^+$ and Al$_{14}$H$^-$ are very similar, the reactivity changes radically. The addition of one H atom turns spin-forbidden reactions into spin-allowed reactions and vice versa; thus rates of reactions with an even number of aluminum atoms are strongly increased, and rates of reactions with odd numbers of aluminum atoms are conversely strongly decreased.

Furthermore, we developed a model that allows us to make predictions on the trends in O$_2$ reactivity within a small number of similar metal atom clusters. In this simple model, the formal oxidation of the metal cluster anion, M$_x$~,~ to the cluster cation (e.g., Al$_{14}$~ to Al$_{14}$^+) determines the $\Delta E^f$ value and therefore is responsible for the differing reactivity of the clusters.

To summarize, the quantification of the rate coefficients for a small number of Al$_{14}$~ and Ga$_{14}$~ clusters in the size vicinity of the exceptional Al$_{13}$/Ga$_{13}$~ species in principle seems to allow a deeper insight into all reactions of O$_2$ with metal atom clusters and possibly also with surfaces of bulk metals; that is, also small changes within the geometric structure of surfaces will change the reactivity. Therefore, our results may also be of fundamental interest for many catalytic processes on metal surfaces where the addition or substitution of a single atom can change the reactivity dramatically.

In our ongoing experiments, we plan to quantify the spin-forbidden reactions of O$_2$ with Al$_{15}$ and Ga$_{13}$ clusters via well-defined excitation of the clusters to overcome the reaction barrier during the spin transitions. These results will be published in a separate paper.22

### EXPERIMENTAL SECTION

All experiments were carried out in a commercial FT-ICR mass spectrometer (Ionspec, Ultima) equipped with a 7 T actively shielded magnet (Cryomagnetics, Oak Ridge, TN, USA). Since the experimental setup and methodology was described elsewhere in detail,6,18,44 only the essentials are given here.

Negatively charged aluminum and gallium clusters (Al$_{14}$~ and Ga$_{14}$~) were generated by laser desorption from LiAlH$_4$ and GaN, respectively,25 where the commercial MALDI (matrix-assisted laser desorption/ionization) source of the FTICR-MS was used (narrow laser, $\lambda = 337.1$ nm, pulse energy = 300 mJ).25 After cluster formation, the ions were transferred into a cylindrical ICR cell via a quadrupole ion guide. To ensure efficient ion trapping (gas assisted dynamic trapping) and translational cooling of the cluster ions, argon (Argon 6.0, Baso Schöberl GmbH & Co. KG) was admitted into the cell with a pulsed valve (General Valve) at a pressure of around 1 $\times$ 10$^{-4}$ mbar for ~1 s. For the study of ions with one particular mass-to-charge ratio (e.g., $m/z = 381.77$ for Al$_{14}$~), the species were isolated by the SWIFT (stored waveform inverse Fourier transform) excitation technique.47 A second thermalization step was carried out in some cases to prevent possible (re)excitation of the ions due to the isolation process and to ensure thermal conditions. Because the second thermalization step did not change the measured rate coefficient within the experimental error, we conclude that ion (re)excitation by the SWIFT method can be neglected.

### QUANTUM CHEMICAL CALCULATIONS

The theoretical studies concerning the kinetics are analogous to those presented recently.33 It should be noted that interpretation of experimentally observed rate coefficients by computations demand clear knowledge of the potential energy surface with accurate estimation of threshold energies of the various intermediates, which in turn depend on the computational method; therefore we use reaction energies as a guide to understand the reactivity of the various clusters presented here.

All the calculations were performed using the generalized gradient approximation (GGA) within the framework of the DFT. The gradient-corrected exchange and correlation functionals due to Becke-Perdew were employed here.48 Split valence basis set supplemented with polarization functions was used for all the atoms.49 The computations were carried out using the Turbomole software.49 In the self-consistent field (SCF) calculations, the density and energy tolerances were set to 10$^{-6}$ e/bohr$^3$ and 10$^{-6}$ hartree, respectively. In the geometry optimization, all the structural parameters were fully optimized without any symmetry constraints, with an energy convergence of 10$^{-6}$ hartree and a maximum gradient of 10$^{-4}$ hartree/bohr. The lowest and other higher energy isomers of all oxide clusters were obtained using an unbiased systematic structure search based on genetic algorithm method.50 In this procedure, all the structures generated either through initial population or cross breeding were fully optimized without any constraints using the same methods mentioned above.

### ASSOCIATED CONTENT

#### Supporting Information

Quantum chemical calculations, structures, and energies (eV) and further experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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### REFERENCES


(5) If the Cl$_2$ partial pressure is low and the temperature of the Al metal is about 700 °C, AlCl molecules are formed first, which are afterwards oxidized to AlCl$_3$: Al + ^1/2Cl$_2$ → AlCl$_3$; AlCl$_3$ + Cl$_2$ → 2AlCl$_3$ (see ref 6).


(10) Based on the same arguments Ag2O2+ species were detected in the gas phase during detailed mass spectrometric and theoretical investigations recently.11


(12) The similarity of the Al13− cluster to the bulk metal regarding thermodynamics is based on the very special electronic structure of this cluster (spherical jellium model with 40 valence electrons) as well as on its topological similarity concerning the coordination number. In both cases, a central Al atom is surrounded by 12 other Al atomsicosahedrally arranged in Al13+ and cuboctahedrally arranged in the metal. Therefore, reactions of the Al13− are model reactions for those of the bulk metal, if the amount of energy necessary to remove two Al atoms from an Al13− cluster is compared with the energy change in the case of the bulk metal:13 Al13− + 2Al(g) ΔHf = +698 kJ mol−1 (calcld); 2Al(g) → 2Al(g) ΔHf = +654 ± 8 kJ mol−1 (expt). Taking into account the usual error margin of DFT calculations, the energy needed for the removal of two Al atoms either from an Al13− cluster or from the bulk Al metal is almost identical. Here Al atoms form the energetically equivalent reference system, and therefore all reactions of Al13− clusters and Al metal should be very similar with respect to their energy balance.


(19) The hindered reactivity of O2 with Al13− in a mixture of other Aln− clusters has been studied in recent papers, where also the unexpected stability has been discussed.20,21


(25) The generation of Ga3+ clusters via laser desorption of solid GaN has successfully been applied in our laboratory for many years. Koch, K. Metalloide Cluster in der Gasphase – FT/ICR-massenspektrometrische Untersuchungen, Dissertation, Universität Karlsruhe, 2005. However, this method has not been published before.

(26) The formation of Alm− clusters by irradiation of AlN was not successful, which seems plausible due to its higher thermodynamic stability; enthalpies of formation, ΔHf(AlN) = −318 kJ mol−1, ΔHf(GaN) = −109 kJ mol−1.2


(28) This accelerating process between the 3O2 molecule and the metalloide cluster in the gas phase is immediately followed by a strongly exoergic step; that is, these reactions proceed spontaneously. However, this hypothesis has to be
ruled out, because the energy of a hypothetic magnetic interaction is far below the thermal energy of the interacting species. 

(41) In step C, only Al−O/Ga−O single bonds are formed like those in the gaseous reaction products Al−O−Al and Ga−O−Ga, respectively. For these linear molecules, bond energies of 5.35 eV (Al₂O) and 4.59 eV (Ga₂O) are known from experimental data. ²,³

(42) Our simple model is also in line with the hindered ³O₂ reaction of Ag₁₃⁻ described recently.¹¹ The formation of neutral Ag₁₃ (EA) (see Figure 3) requires the largest energy of all Ag⁻ clusters, that is, the lowest energy (∆Eₓ = −0.5 eV) is gained by the formation of the end-on [O₂Ag₁₃]⁻ cluster, and consequently the electron transfer to an O₂⁻ species must overcome a high barrier, which is in line with an extremely slow reaction.


