Hydrogen-Promoted Oxygen Activation by Free Gold Cluster Cations

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Abstract: Small gas-phase gold cluster cations are essentially inert toward molecular oxygen. Preadsorption of molecular hydrogen, however, is found to cooperatively activate the binding of \( \text{O}_2 \) to even-size \( \text{Au}_x^+ \) \((x = 2, 4, 6) \) clusters. Measured temperature- and reaction-time-dependent ion intensities, obtained by ion trap mass spectrometry, in conjunction with first-principles density-functional theory calculations, reveal promotion and activation of molecular oxygen by preadsorbed hydrogen. These processes lead to the formation of a hydroperoxo intermediate on \( \text{Au}_4^+ \) and \( \text{Au}_6^+ \) and culminate in the dissociation of \( \text{O}_2 \) via the release of \( \text{H}_2\text{O} \). Langmuir–Hinshelwood reaction mechanisms involving the coadsorption of both of the reactant molecules are discussed for both cluster sizes, and an alternative Eley–Rideal mechanism involving hydrogen molecules adsorbed on a \( \text{Au}_6^+ \) cluster reacting with an impinging gaseous oxygen molecule is analyzed. Structural fluctuation of the gold hexamer cation, induced by the adsorption of hydrogen molecules, and resulting in structural isomerization from a ground-state triangular structure to an incomplete hexagonal one, is theoretically predicted. Bonding of \( \text{H}_2 \) on cationic gold clusters is shown to involve charge transfer to the clusters. This serves to promote the bonding of coadsorbed oxygen through occupation of the antibonding \( 2\pi^* \) orbitals, resulting in excess electronic charge accumulation on the adsorbed molecule and weakening of the \( \text{O}--\text{O} \) bond. The theoretical results for hydrogen saturation coverages and reaction characteristics between the coadsorbed hydrogen and oxygen molecules are found to agree with the experimental findings. The joint investigations provide insights regarding hydrogen and oxygen cooperative adsorption effects and consequent reaction mechanisms.

1. Introduction

The catalytic properties of gold particles that emerge when their dimensions are reduced to the nanoscale continue to be a subject of great research interest and an area of discovery.1–8 Studies of catalysis by gold nanoparticles are part of the fast-developing field of nanocatalysis4 where emphasis is placed on new size-dependent chemical reactivity and catalytic properties that are found when the size of metal catalyst particles reaches the ultimate nanocluster regime, that is, clusters comprised of up to 10 or 20 atoms, characterized by sizes of up to 1 nm.2,5,6 (see also the discussion in ref 7). Indeed, in this size regime “small is different”8 in an essential manner that could not have been anticipated through extrapolation of knowledge obtained for larger sizes, and where scaling arguments do not apply. In this non-scalable size regime material aggregates may be regarded as “zero-dimensional” quantum dots whose physical and chemical properties are determined by quantum size effects that originate from the spatial confinement of the electrons. In such nanoclusters a dominant fraction of the atoms are undercoordinated (that is, they are situated in a nonbulk environment), and thus, they are expected to exhibit enhanced chemical reactivity. Furthermore, as commonly found in molecular systems, nanoscale clusters may exhibit a number of structural isomers, and transformations from one isomeric form to another may be induced thermally or chemically (i.e., due to the influence of adsorbates and/or interactions with reactant molecules); such structural effects play an important role in nanocatalysis, and they have been termed “dynamical fluctuationality”, describing structural variations that may occur in the course of chemical reactions.9 As a consequence of the above discussion we conclude that to elucidate and understand the electronic and structural factors that control nanocatalytic activity one must focus on experimental and theoretical investigations that highlight the size-dependent correlations between

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the electronic structure and geometrical arrangement of the atoms (including dynamic fluctional distortions).

During the past decade it has been found through experimental and theoretical investigations (performed mostly on clusters supported on the surfaces of metal oxides) that the chemical properties and catalytic activity of gold depend on, and can be controlled by, several factors, including: (i) the size and dimensionality of the gold nanoclusters, (ii) the chemical identity (composition) and structure of the supporting substrate (crystalline or amorphous, surface crystallography, film thickness, and degree of perfection, i.e., the presence, or absence, of surface defects, commonly F-center oxygen vacancies), and (iii) the charge state of the catalytic metal cluster, which may depend on the nature and properties of the support (with charging by electrons originating from surface F-centers playing an important role in the case of supported clusters). These studies have revealed that in heterogeneous catalysis the support (most commonly a metal oxide surface) is often an integral active part of the catalytic system and that the catalytic activity may be controlled through substrate manipulations (for a most recent study see ref 7).

A significant number of recent investigations focused on gold-based oxidation nanocatalysts, which can be operated at low temperatures and are able to efficiently activate molecular oxygen; these properties are of special importance for the development of environmentally sustainable catalytic processes. While the partial oxidation of hydrocarbons is characterized by remarkably high product selectivity, the application of gold particle catalysts is hampered by a poor yield of such processes and by the need to supply equimolar amounts of hydrogen in addition to molecular oxygen. Despite the great interest in this reaction, the role of hydrogen in the oxidation reaction mechanism is largely not understood.

Most explorations pertaining to catalysis by gold focused on surface-supported gold catalysts. As aforementioned, in these investigations the influence of the substrate support plays an important role in controlling the catalytic activity, and consequently, the observed reactivity consists of a convolution of the gold cluster and support properties. Therefore, to interrogate the intrinsic chemical reactivity of gold nanocluster catalysts (in addition to our long-standing interest in gas-phase nanocatalysis), we focus here on free, gas-phase, gold clusters. Previous experimental studies of the reactions of free gold clusters with molecular oxygen revealed that the reactivity of anionic Au\(^{+}\) (x = 1) clusters exhibits a pronounced odd-even alternation, with even-size clusters being reactive while odd-size clusters were found to be essentially inert. Such odd-even alternations were also found in theoretical investigations.

Theoretical calculations also predict binding of O\(_2\) to cluster cations Au\(^{+}\). However, oxidation products of cationic gold clusters (containing, most likely, atomic oxygen) have only been observed experimentally when oxygen was added to the highly reactive and strongly nonthermal laser plasma generated in a laser ablation cluster source. Here we find the gold cations Au\(^{x+}\) (x = 2–7) to be nonreactive toward molecular oxygen under thermal reaction conditions, in agreement with earlier investigations under comparable conditions.

For molecular hydrogen the dependence of the reactivity on the gold cluster charge state is reversed, with the anionic clusters Au\(^{-}\) found to be nonreactive. In contrast, the adsorption of H\(_2\) on Au\(^{+}\) has been observed under multicolission conditions in a flow-tube reactor experiment, while the process does not occur under single-collision conditions at room temperature.

In this paper we present experiments and first-principles density-functional theory (DFT) calculations on gas-phase reactions of small gold clusters, aiming at elucidation of the role of hydrogen in the activation of molecular oxygen. Positively charged gold clusters Au\(^{+}\) (x = 2–7) were chosen because electronic factors and experimental data suggest them to be most suitable for promoting the oxidation of unsaturated hydrocarbons. Our investigations show that, although small gas-phase gold cluster cations are known to be inert toward molecular oxygen, the preadsorption of molecular hydrogen cooperatively enables the adsorption of O\(_2\) on the even-size Au\(^{+}\) clusters. Moreover, investigations of the temperature- and reaction-time-dependent ion intensities, occurring in an octopole ion trap under multicollision conditions, indicate that hydrogen promotes the activation of molecular oxygen on Au\(^{+}\) and Au\(^{2+}\), leading to the dissociation of O\(_2\) at temperatures as low as 200 K. The detailed mechanisms of hydrogen-induced oxygen activation, involving formation of a hydroperoxo transition complex and the elimination and desorption of H\(_2\)O, are revealed with the use of DFT calculations.

The paper is organized as follows. In section 2 we describe the experimental setup, data evaluation procedure, and theoretical methods. Our results are presented in section 3, with the experimental findings described first in section 3. The theo...
ermal results are given in section 3.2, with an analysis of hydrogen and oxygen binding on Au$_x^+$ and Au$_x^-$ given in section 3.2.1.1 and section 3.2.1.2, respectively. Reaction pathways proceeding via Langmuir—Hinshelwood or Eley—Rideal mechanisms are displayed and analyzed in section 3.2.2 (with reactions on Au$_x^+$ discussed in section 3.2.2.1 and reactions on Au$_x^-$ in section 3.2.2.2); our discussion includes analysis of the formation of transition-state complexes and interaction intermediates leading to the dissociation of O$_2$. The theoretical results agree well with the experimental findings, and they provide useful insights pertaining to the nature of bonding, activation, and reactions of coadsorbed hydrogen and oxygen on small gold cation clusters. We summarize our results in section 4.

2. Methods

2.1. Experimental Setup. The experimental setup used in the study of the Au$_x^+$(x = 2–7) cluster reactions consists of a variable-temperature radio frequency (rf) octopole ion trap inserted into a low-energy ion beam assembly of two quadrupole mass spectrometers and two ion guides. Since the general experimental setup is described in detail elsewhere, we limit ourselves here to a brief outline of certain pertinent elements of the experiment.  

Four high-energy xenon ion beams of a CORDIS (cold reflex discharge ion source) simultaneously sputter four metal targets which release small metal clusters, consisting of neutrals and ions, in the size range of a few atoms. Clusters of the desired charge state are introduced into a helium-filled quadrupole, which serves to collimate and thermalize the hot cluster ions. Subsequently, clusters with the desired size are selected from the beam by a mass-selective quadrupole filter and are steered through an ion-guiding quadrupole into the home-built octopole ion trap. The trap is prefilled with helium (at about 1 Pa total pressure) and the reactive gases (H$_2$ and O$_2$). The absolute pressure inside the trap is measured by a Baratron gauge (MKS, type 627B, regulation and detection accuracy 0.01 Pa). The ion trap is attached to a helium cryostat that allows for temperature adjustment in the range between 20 and 300 K. Thermal equilibration of the clusters is achieved within a few milliseconds (about 10$^5$ collisions) under our experimental conditions, while the clusters are stored for a considerably longer time, typically between 0.1 s and several seconds. After the chosen reaction time, i.e., storage time, $t_R$, all ions, intermediates, and products are extracted by applying a pulsed bias potential to the exit lens of the ion trap. The ion distribution is subsequently analyzed by a second quadrupole mass filter. To account for a slightly asymmetric mass peak shape occurring at very low ion intensities in our apparatus, the raw data have been deconvoluted, and the resulting mass peak shape occurring at very low ion intensities in our apparatus, the raw data have been deconvoluted, and two ion guides. Since the general experimental setup is described in detail elsewhere, we limit ourselves here to a brief outline of certain pertinent elements of the experiment.

2.2. Data Evaluation. To interpret and understand the experimental data, in particular with respect to the temperature dependencies, it is necessary to briefly outline the reaction models underlying the measured processes. As an example, the straightforward association reaction

$$\text{Au}^+_x + \text{H}_2 \rightarrow \text{Au}^+_x \text{H}_2^+ \quad (1)$$

is discussed in the following. Note that the models are exactly the same for the molecular oxygen coadsorption discussed later in this paper.

Since the total pressure inside the ion trap is about 1 Pa, and therefore the experiments are performed in the kinetic low-pressure regime, a Lindemann-type mechanism has to be considered for each reaction step. Furthermore, the concentrations of the reactive gases, as well as the buffer gas in the ion trap, are orders of magnitude larger than the Au$^+$ concentration, and a steady flow of the reactants is ensured. This permits the postulation of pseudo-first-order kinetics for all proposed reaction steps.

The details of reaction 1 are described by the Lindemann energy transfer model for association reactions, which is presented by the following equations:

$$\text{Au}^+_x + \text{H}_2 \rightarrow \text{Au}^+_x \text{H}_2^+ \quad (2a)$$

$$(\text{Au}^+_x \text{H}_2^+*) + \text{He} \rightarrow \text{Au}^+_x \text{H}_2^+ + \text{He}^* \quad (2b)$$

The reaction model includes three elementary steps: (1) the formation of an energized complex (Au$^+_x$H$_2^*$) ($k_a$) and (2) the potential unimolecular decomposition back to the reactants ($k_b$), in competition with (3) a stabilizing energy transfer collision ($k_w$) with helium buffer gas or also with other reactant molecules (omitted in eq 2b for the sake of clarity). The ion—molecule association rate constant, $k_a$, and the final stabilization rate constant, $k_b$, are well represented by ion—molecule collision rate coefficients as specified by the Langevin theory. According to this theory, ion—molecule reactions are basically interactions between a charge and an induced dipole and thus exhibit no activation barrier and hence no temperature dependence of the rate coefficients. Therefore, any observed temperature dependence must be contained in the unimolecular decomposition rate constant, $k_b$. The activation barrier of this unimolecular decomposition results in a negative temperature dependence for the overall reaction (eq 1). This means, vice versa, that whenever a negative temperature dependence is observed in the experiments, a barrier-free reaction pathway can be assumed. In contrast, a positive temperature dependence would indicate an activated reaction mechanism.

2.3. Computational Methods. In explorations of the atomic arrangements and electronic structures of gold cluster cations, the binding characteristics and structures of molecules adsorbing on such clusters, and the mechanisms of reactions catalyzed by these clusters, we have used first-principles DFT calculations. In particular, we employed the Born—Oppenheimer (BO) spin density functional (SDF) molecular dynamics (MD) method, BO-SDFMD, with norm-conserving soft pseudopotentials (including a scalar relativistic pseudopotential for Au) and the generalized gradient approximation (GGA) for electronic exchange and correlations. In these calculations we have used a plane wave basis with a kinetic energy cutoff of 62 Ry. The BO-SDF-MD method is particularly suitable for investigations of charged systems since it does not employ a supercell (i.e., no periodic replication of the ionic system is used). Structural optimizations were performed using a conjugate-gradient-like method. Previous investigations of gold clusters (as well as other clusters) and their chemical reactivity using the above methodology have yielded results in good agreement with

experimental findings. We remark here that such calculations have been shown to give very accurate bond lengths (up to 1% too long) and reaction barriers that are accurate to within 25%–30% (usually too low; see p 87 of ref 4).

For each of the cluster systems that we consider in this study we explored several reaction mechanisms corresponding to the various model catalyst systems investigated in the experiments. The reaction profiles (pathways) that we present were obtained via first-principles quantum calculations described above. In these calculations a reaction coordinate was judiciously chosen; the reaction coordinate may consist of several geometrical parameters pertinent for the studied mechanism; for example, a reaction coordinate may entail at a certain stage of the reaction the distance between two reacting atoms, e.g., the distance between an O atom of an adsorbed oxygen molecule and the nearest H atom of a coadsorbed hydrogen molecule, while at a subsequent stage the pertinent reaction coordinate may correspond to the rotation angle of a chosen molecular group. For each value of the reaction coordinate, the total energy of the system was optimized through unconstrained relaxation of all of the other degrees of freedom of the system (reactant molecules and gold cluster atoms). The reaction profiles were obtained via repeating such calculations for various values of the chosen reaction coordinate; we note that no distance (or angle) scales are attached to the horizontal axes of the reaction profiles (see Figures 11–14). These calculations yield results that are the same as, or close to, those obtained by other methods (e.g., the nudged elastic band and variants thereof; see the discussion on pp 89 and 90 in ref 4).

3. Results

3.1. Experimental Results. In the first set of experiments we investigated the reaction of $\text{Au}_x^+$ ($x = 2 – 7$) toward pure hydrogen and oxygen independently. As already mentioned in the Introduction, in complete agreement with previous studies under thermal conditions,8,17,25,26 small gold cluster cations are found to be entirely unreactive toward molecular oxygen at any temperature investigated. In contrast, a distinct temperature- and cluster-size-dependent reaction behavior toward molecular hydrogen is observed.

3.1.1. $\text{H}_2$ Adsorption. Only products of the stoichiometry $\text{Au}_x\text{H}_y^+$ ($y = 2, 4, ..., 12$) are detected. Although it cannot be determined on the basis of our experimental results alone whether hydrogen retains its molecular structure, coordinates to the cluster with both hydrogen atoms,38 or even dissociates on the cluster as previously predicted theoretically,15 coadsorption experiments with nitrogen indicate that $\text{H}_2$ is adsorbed molecularly, because $\text{N}_2$ and $\text{H}_2$ are found to compete for the same adsorption sites and reactant partial-pressure-dependent adsorbate exchange is observed.

At a reaction temperature of $T_R = 300$ K none of the investigated clusters form any stable reaction products with molecular hydrogen, except $\text{Au}_3^+\text{H}_2$, which adsorbs up to three $\text{H}_2$ molecules at a reaction time $t_R = 0.5$ s. Cooling to 200 K changes the reaction behavior dramatically. While the gold dimer is still unreactive, $\text{Au}_5^+$ and $\text{Au}_7^+$ adsorb up to three, $\text{Au}_6^+$ and $\text{Au}_8^+$ up to four, and $\text{Au}_9^+$ up to two hydrogen molecules. At this temperature the reactions of $\text{Au}_5^+$, $\text{Au}_7^+$, and $\text{Au}_8^+$ are already so fast that even at the shortest measured reaction time ($t_R = 0.1$ s) no pure metal cluster signal can be observed. Further lowering the temperature to 100 K leads to an almost instantaneous size-dependent hydrogen saturation of the clusters. Figure 1 shows the maximum (saturation) number of adsorbed hydrogen molecules at $T_R = 100$ K.

Figure 1. Cluster-size-dependent hydrogen saturation at $T_R = 100$ K and minimum-energy structures of the investigated cluster sizes41 (see also Figures 6 and 8–10). “Corner” site atoms are indicated by filled circles. For the case of $\text{Au}_6^+$ the two lowest energy isomers are displayed with the nontriangular incomplete hexagonal (ih) isomer being 0.19 eV higher in energy than the triangular (t) one (see Figure 9).

Up to the gold pentamer these cluster-size-dependent hydrogen saturation levels are in perfect agreement with previous experiments by Cox et al.;17,26 in the earlier experiment saturation was not reached only for $x = 6$ and 7. We note that our observed correlation between the $\text{H}_2$ saturation numbers and the number of “corner” atoms in the clusters (see the discussion below) agrees with earlier findings obtained from saturation measurements for $\text{Au}_{32}^+$ with CO,39 methane (CH$_4$)$_{32,40}$ and ethylene (C$_2$H$_4$)$_{40}$ as long as the gold clusters do not experience adsorbate induced structural changes.39

To analyze possible binding sites, we also display the reported41 (see also Figures 6 and 8–10) minimum-energy structures of $\text{Au}_x^+$ in Figure 1. Generally, $\text{H}_2$ acts as an electron-donating ligand to transition-metal cations,12 and consequently, the binding of hydrogen to a particular site of the gold cluster cation is expected to correlate with the localization of the cluster lowest unoccupied molecular orbital (LUMO).43 Recent DFT calculations indicate that the LUMO of the bare cluster is primarily located on corner atoms, where it protrudes most into the vacuum.28 As a result, hydrogen will preferably bind to corner atoms, whereas no adsorption on central atoms or cluster flat faces is expected.28 Indeed, the results of our measurements (as well as our DFT calculations for $\text{Au}_x^+$ and $\text{Au}_5^+$; see below) show for all the $\text{Au}_x^+$ clusters, except $\text{Au}_7^+$, saturation numbers of adsorbed hydrogen molecules that equal the number of gold atoms positioned at corner sites in the corresponding ground-state (lowest energy) geometries (cf. Figure 1; see also Figures 6 and 8–10). Only in the case of $\text{Au}_6^+$ the maximum number of $\text{H}_2$ molecules agrees better with the higher energy isomeric structure (the nontriangular, incomplete hexagonal (ih) geometry displayed in Figure 1). Indeed, our DFT calculations show that the $\text{Au}_6^-$ cluster undergoes, upon hydrogen adsorption, isomerization from a triangular ground-state geometry of the bare cluster to the nontriangular, incomplete hexagonal, geometry (see Figures 9 and 10).


observed in the mass spectra: while all the odd cluster sizes (in the cluster cation (the mass spectral peaks correspond to the number of gold atoms

3 displays ion mass distributions obtained after the Au ions were trapped for adsorption, as discussed in section 2.

To further illustrate the temperature dependence of the hydrogen adsorption to the gold cluster cations, we display in Figure 2 the hydrogen adsorption on Au\textsuperscript{+} at a fixed reaction time \( t_R = 0.5 \text{ s} \). Since for this representation one should consider in addition to the temperature dependence of the reaction rate (and thus the extent of reaction at a given temperature) the amount of adsorbed hydrogen molecules, the height of the bars \( Y^{\text{hydr}} \) reflects, for each cluster size, the ratio of the actual hydrogen coverage to the maximum (saturation) hydrogen coverage, calculated by

\[
Y^{\text{hydr}} = \frac{\sum_{i \text{ad}} I_i}{\sum_{i \text{prod}} I_{\text{prod}}^{\text{max}}} \times 100\%
\]

where \( I_i \) denotes the intensity of the product peak corresponding to \( i \) adsorbed hydrogen atoms, \( I_{\text{prod}} \) is the sum of the intensities of all products, and \( y_{\text{max}} \) denotes the saturation number of adsorbed hydrogen atoms. From the bar charts in Figure 2 it is apparent that for all cluster sizes hydrogen adsorption is accelerated by decreasing the reaction temperature. This negative temperature dependence indicates a barrier-free hydrogen adsorption, as discussed in section 2.

3.1.2. Coadsorption of O\textsubscript{2} and H\textsubscript{2}. Next, at a reaction temperature of \( T_R = 100 \text{ K} \) a mixture of the reactive gases \( \text{H}_2 \) and \( \text{O}_2 \) was introduced into the ion trap at a ratio of 1:2. Figure 3 displays ion mass distributions obtained after the Au\textsuperscript{+} clusters were trapped at 100 K for \( t_R = 0.1 \text{ s} \); the labels \((x,y,z)\) next to the mass spectral peaks correspond to the number of gold atoms in the cluster cation \( (x) \) and the numbers of adsorbed hydrogen \((y)\) and oxygen \((z)\) atoms. A striking odd—–even alternation is observed in the mass spectra: while all the odd cluster sizes \((x = 3, 5, \text{ and } 7)\) reach almost instantaneously their hydrogen saturation level as in the case of pure hydrogen exposure (see Figure 1), with no measurable coadsorption of oxygen, the even-size clusters \((x = 2, 4, \text{ and } 6)\) do not achieve complete hydrogen saturation and exhibit instead cooperative coadsorption\textsuperscript{10,44} of one oxygen molecule \((z = 2)\) in addition to hydrogen. The coadsorption of multiple \( \text{O}_2 \) molecules has not been observed even at higher \( \text{O}_2 \) pressures and extended reaction times.

As molecular oxygen does not react with Au\textsuperscript{+}, hydrogen preeadsorption is responsible for the activation of the gold clusters to enable cooperative oxygen coadsorption. Cooperative coadsorption is known to be an important reactivity-promoting process for small metal clusters and nanoparticles.\textsuperscript{13,44}

In a simple valence electron structure model the odd—–even alternation in the \( \text{O}_2 \) coadsorption can be attributed to the fact that odd-size gold cluster cations exhibit a closed-shell valence electron structure leading to a low binding energy for the hydrogen-promoted oxygen adsorption.\textsuperscript{18,20,29,45} In contrast, even-size gold cluster cations possess an unpaired valence electron that, upon hydrogen activation, may interact with the two unpaired electrons occupying the \( 2\pi_g^* \) antibonding orbital of the oxygen molecule, resulting in stable complexes; the mechanism of reaction between charged gold clusters and \( \text{O}_2 \) involving the antibonding molecular orbitals of the oxygen molecule, has been elucidated for the case of gold anions, Au\textsuperscript{−}, where (in the context of the oxidation of CO) it has been shown that this bonding mechanism serves to weaken (i.e., activate) the \( \text{O}–\text{O} \) bond of the adsorbed oxygen molecule.\textsuperscript{2,3,9,10,12} The use of this picture for explaining the mechanism of the observed promotion of the reactivity of the cluster cations toward \( \text{O}_2 \), occurring through the preeadsorption (or coadsorption) of hydrogen, will be addressed below when we discuss our theoretical calculations.

We focused in the experiments, as well as in the theoretical investigations, on the even-size cluster ions \( \text{Au}_n^{+} \) and \( \text{Au}_6^{+} \), because these clusters are the only investigated clusters that exhibit hydrogen-induced oxygen coadsorption at temperatures


above 200 K, which eventually leads to the dissociation of O₂ on the clusters. Further experimental information can be gained from temperature- and reaction-time-dependent measurements.

Representative product mass spectra of Au₄⁺ and Au₆⁺ obtained under various reaction conditions are assembled in Figure 4; the data in the left (a−f) (right (g−l)) column correspond to the Au₄⁺ (Au₆⁺) cluster, respectively. The topmost traces (a, g) show the pure mass signals of the metal cluster in the absence of any reactive gases. Mass spectra obtained after the addition of hydrogen at a reaction temperature of 100 K are depicted in the second topmost traces (b, h). As detailed above, and in agreement with previous experiments, under multicollision conditions H₂ is found to adsorb on Au₄⁺ clusters, leading to the maximum coverage species Au₄H₉⁺ (mass peak in (b) labeled (4,8,0)) and Au₆H₁₀⁺ (mass peak in (h) labeled (6,10,0)); the corresponding saturated coverage configurations (Au₄H₉⁺ and Au₆H₁₀⁺), with one H₂ molecule attached to each of the undercoordinated corner Au atoms, are shown in Figures 6a, 8a, and 10a, with the average binding energies per H₂ molecule being 0.53 and 0.38 eV for Au₄⁺ and Au₆⁺, respectively.

Adding both H₂ and O₂ to the ion trap at 100 K yields the coadsorption products Au₄H₆O₂⁺ and Au₆H₄O₂⁺ even at a very short reaction time t₀ = 0.1 s (Figure 4; see the mass peak labeled (4,6,2) in trace (c) and the one labeled (6,6,2) in trace (i); cf. also Figure 3). When the reaction time is kept constant at 0.1 s, but the ion trap is heated to 200 K, the signal intensity of the coadsorption product Au₄H₆O₂⁺ decreases (Figure 4, trace d). In addition, under these conditions, Au₄H₄⁺ is detected instead of Au₄H₆⁺. Increasing the reaction time to 0.5 s does not notably change the intensity of these products (trace e). Also no additional products are observed at longer reaction times. A further increase in temperature to 300 K, however, alters the product mass spectrum drastically. From trace f it is apparent that no hydrogen adsorption products are observed anymore; instead the bare Au₄⁺ signal reappears together with a new mass peak corresponding to the mass of Au₄H₂O⁺ containing a single oxygen atom. In contrast, the Au₄H₂O₂⁺ peak decreases in relative intensity, reflecting the dissociation of the initially coadsorbed O₂ molecule.

The activation and dissociation of the coadsorbed oxygen molecule with increasing temperature is even more apparent for Au₆⁺. In this case, the coadsorption product Au₆H₄O₂⁺ is the sole mass signal at 100 K, when O₂ and H₂ are admitted to the trap (Figure 4, trace i). At the same reaction time of 0.1 s, but at 200 K, Au₆H₄O₂⁺ is detected in addition to Au₆H₆O₂⁺ as well as Au₆H₄⁺ (trace j). Trace k in Figure 4, obtained at an increased reaction time of 2.0 s and 200 K, reveals that Au₆H₆⁺, Au₆H₄O₂⁺, and Au₆H₆O₂⁺ are still apparent while an additional mass peak corresponding to Au₆H₂O⁺ emerges. Hence, in the case of Au₆⁺ the dissociation of the coadsorbed O₂ already proceeds at 200 K. Further heating the ion trap to 300 K causes both Au₆H₆⁺ and the coadsorption products Au₆H₂O⁺/Au₆H₆O₂⁺ to vanish. Only Au₆H₂O⁺, containing a single oxygen atom, is detected (trace l) along with the unreacted bare Au₆⁺ cluster.

The temperature dependence of the Au₄H₂O⁺ and Au₆H₂O⁺ product formation is further detailed in Figure 5 in a bar graph representation and shows the same behavior as in the case of Au₄⁺. The intensity of the product signal, I, corresponding to products of the stoichiometries Au₄H₂O⁺ (light gray bars) and Au₆H₂O⁺ (dark gray bars) relative to the intensity of all products, I_{prod} (excluding the pure metal cluster peak), is calculated and plotted as the reaction yield, Y^{OX}, as a function of the reaction temperature. Note that at a given temperature the sum of the heights of the light and dark gray bars may not necessarily reach 100%, since the adsorption of hydrogen by the cluster, which increases the total product intensity, is not necessarily accompanied by oxygen coadsorption.

From Figure 5 we observe that for both Au₄⁺ and Au₆⁺ clusters the reaction yield, Y^{OX}, of Au₄H₂O⁺ products (dark gray

\[
Y^{OX} = \frac{I}{I_{prod}} \times 100\%
\]
Activation barrier for the dissociation of $O_2$. As we discuss a barrier-free $O_2$ adsorption on the cluster. In contrast, the energy of $O_2$ onto the $Au_4(H_2)_3$ cluster. c denotes the effect of coadsorption excess electronic charge, and pink ones correspond to charge deficiency.

Note that charge difference plot $c$ pertains to the effect of coadsorption cluster cation with the adsorbed molecules. Blue regions correspond to charge excess in the atomic structures, with Au atoms depicted by yellow balls, hydrogen atoms by blue balls, and oxygen atoms by red balls. The numbering scheme of the atoms is displayed in (c). All the cases shown correspond to molecular (nondissociative) adsorption.

Figure 6. Difference charge density isosurfaces (encompassing 90% of the charge) for (a) the saturation coverage cluster $Au_4(H_2)_4^{+}$, (b) $Au_4(H_2)_3(3c,2c,2c)^{+}$, and (c, d) $Au_4(H_2)_3(3c,2c,2c)O_2(3c)^{+}$. The charge density differences are calculated as (a) $\rho_{\text{tot}} - \rho[\text{Au}^+] - \rho[\text{H}_2]$, (b) $\rho_{\text{tot}} - \rho[\text{Au}^+] - \rho[\text{H}_2]$, (c) $\rho_{\text{tot}} - \rho[\text{Au}^+] - \rho[\text{H}_2]$, and (d) $\rho_{\text{tot}} - \rho[\text{Au}^+] - \rho[\text{H}_2]$. $\rho_{\text{tot}}$ is the total charge density of the gold cluster and the other two ($d(H-H) = 0.82$ Å) of the cluster and the other two ($d(H-H) = 0.815$ Å) are normal to it; the $Au-Au$ distances at $H_2$ saturation are $d(Au(1)-Au(2)) = 2.75$ Å and $d(Au(2)-Au(3)) = 2.62$ Å. As seen from Table 1, the adsorption energy depends on the number of adsorbed molecules and on the adsorption sites. For example, adsorption of a single $H_2$ molecule on a 2-fold-coordinated (2c) Au atom (e.g., atoms 1 and 4 in Figure 6c) occurs with an energy $E_d(H_2; 2c) = 0.50$ eV, while for adsorption at a 3-fold-coordinated (3c) gold atom (e.g., atoms 2 and 3 in Figure 6c) the binding energy is higher, $E_d(1H_2; 3c) = 0.62$ eV. At saturation (4$H_2$) the average binding energy per molecule is 0.53 eV, and the adsorption energy of the fourth $H_2$ molecule depends on the adsorption sites of the previously adsorbed three $H_2$ molecules: $\Delta E_d$($H_2; 4) = 0.46$ eV if the previous three occupied the (3c,3c,2c) sites, and $\Delta E_d$($H_2; 4) = 0.52$ eV when the previous three occupied the (2c,2c,3c) sites (see Table 1). Binding of molecular hydrogen to the cluster involves charge donation to the gold atoms, estimated for the saturation case (see the charge density difference plots in Figure 6a, with blue corresponding to excess charge) to be 0.15e (distributed equally on the gold atoms).

The binding of an oxygen molecule to the $Au_4^{+}$ cluster is also nondissociative, although as we discuss below the molecule may dissociate in a process involving energy barriers (as observed experimentally; see Figure 4). The binding of the $O_2$ molecule to the cluster is barrierless (as deduced also from the experiments), it is promoted by coadsorption of molecular hydrogen, and it depends on the adsorption site. We focus here on the only case of molecular oxygen adsorption found experimentally, that is, in stoichiometrical notation $Au_4H_2O_2^{+}$ (labeled (4,6,2) in Figures 3 and 4) and corresponds to the complex $Au_4(H_2)O_2^{+}$. We distinguish two adsorption configurations, where the $O_2$ molecule binds to a 3-fold- and a 2-fold-coordinated Au atom. In the first one (Figure 6c) the $O_2$ molecule is bonded to a 3-fold-coordinated Au atom, while of the bonding sites of the three coadsorbed $H_2$ molecules one is a 3-fold-coordinated Au atom and two are 2-fold-coordinated atoms; i.e., the coadsorption complex may be described as

<table>
<thead>
<tr>
<th>$n$</th>
<th>$E_d(nH_2)$ (eV)</th>
<th>$E_d(nH_2)/n$ (eV)</th>
<th>ads site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.502</td>
<td>0.502</td>
<td>2c</td>
</tr>
<tr>
<td>2</td>
<td>0.621</td>
<td>0.621</td>
<td>3c</td>
</tr>
<tr>
<td>3</td>
<td>1.182</td>
<td>0.591</td>
<td>2c,3c</td>
</tr>
<tr>
<td>4</td>
<td>0.847</td>
<td>0.437</td>
<td>2c,2c</td>
</tr>
<tr>
<td>5</td>
<td>1.605</td>
<td>0.535</td>
<td>2c,2c,3c</td>
</tr>
<tr>
<td>6</td>
<td>1.665</td>
<td>0.555</td>
<td>3c,3c,2c</td>
</tr>
<tr>
<td>7</td>
<td>2.128</td>
<td>0.352</td>
<td>3c,3c,2c</td>
</tr>
</tbody>
</table>

$^{a}$ 2c and 3c denote, respectively, 2-fold- and 3-fold-coordinated Au atoms in the gold tetramer cation. The adsorption energy of the nth $H_2$ molecule can be calculated from $\Delta E(H_2; n) = E_d(nH_2) - E_d((n-1)H_2)$. Energies are given in electron volts.

Hydrogen molecules bind nondissociatively to the tetramer cluster cation in an on-top geometry; see Figure 6a corresponding to saturation coverage, with each of the adsorbed hydrogen molecules attached to a gold atom that is equidistant from the two hydrogen atoms of the adsorbed $H_2$ molecule, $d(Au-H(1)) = 1.88$ Å and $d(Au-H(2)) = 1.88$ Å. At saturation (see Figure 6a), two of the molecules are in the plane ($d(H-H) = 0.82$ Å) of the cluster and the other two ($d(H-H) = 0.815$ Å) are normal to it; the $Au-Au$ distances at $H_2$ saturation are $d(Au(1)-Au(2)) = 2.75$ Å and $d(Au(2)-Au(3)) = 2.62$ Å. As seen from Table 1, the adsorption energy depends on the number of adsorbed molecules and on the adsorption sites. For example, adsorption of a single $H_2$ molecule on a 2-fold-coordinated (2c) Au atom (e.g., atoms 1 and 4 in Figure 6c) occurs with an energy $E_d(H_2; 2c) = 0.50$ eV, while for adsorption at a 3-fold-coordinated (3c) gold atom (e.g., atoms 2 and 3 in Figure 6c) the binding energy is higher, $E_d(1H_2; 3c) = 0.62$ eV. At saturation (4$H_2$) the average binding energy per molecule is 0.53 eV, and the adsorption energy of the fourth $H_2$ molecule depends on the adsorption sites of the previously adsorbed three $H_2$ molecules: $\Delta E_d$($H_2; 4) = 0.46$ eV if the previous three occupied the (3c,3c,2c) sites, and $\Delta E_d$($H_2; 4) = 0.52$ eV when the previous three occupied the (2c,2c,3c) sites (see Table 1). Binding of molecular hydrogen to the cluster involves charge donation to the gold atoms, estimated for the saturation case (see the charge density difference plots in Figure 6a, with blue corresponding to excess charge) to be 0.15e (distributed equally on the gold atoms).

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Au(H2)3(3c,2c,2c)O2(3c)+. The total binding energy of the adsorbed molecules is 2.36 eV (with reference to the ground state of the bare Au+ cluster), and the binding energy of the O2 molecule to the cluster with three H2 molecules preadsorbed to it (i.e., Au(H2)3(3c,2c,2c)+) is 0.76 eV; d(Au−O) = 2.23 Å. In this binding case there is excess electronic charge on the O2 molecule (estimated to be about 0.14e; see Figure 6a, and the molecule is activated with an increased interatomic distance d(O−O) = 1.33 Å (compared to 1.25 Å in the gas-phase isolated molecule).

Interestingly, in the Au(H2)3(3c,2c,2c)+ complex we find that the distribution of the excess electronic charge on the Au atoms (see Figure 6b) differs markedly from that found for the saturation coverage case (Figure 6a). In the present case (Figure 6b), the total excess charge on the gold atoms is estimated to be 0.15e, with 0.09e localized on the bare Au+ cluster and 0.06e on the Au atom of the adsorbed O2 molecule. The spatial distribution of this excess charge is shown in Figure 6a, and the remainder is distributed over the adsorbed O2 molecule.

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eq 5b). We observe that the orbitals that make the largest contribution to the estimator exhibit an antibonding (2π*) character in the vicinity of the adsorbed oxygen molecule (see the right-side region in Figure 7a–c, and compare with Figure 7d); note also the way that this region of the wave function connects to the Au cluster part, showing hybridization of the molecular state with the gold cluster orbitals.

To explore further the promotion effect of hydrogen coadsorption on the binding of an oxygen molecule (and in particular the dependence on the number of coadsorbed H₂ molecules), we consider here O₂ adsorption at a 3-fold-coordinated Au atom (as in Figure 6c discussed above in the context of the maximal number of coadsorbed hydrogen molecules), but, now, in the presence of a single coadsorbed H₂ molecule. We consider two cases: one where the coadsorbed H₂ molecule binds to a 2-fold-coordinated Au atom (as in configuration B shown in Figure 13) and the other where it binds to a 3-fold-coordinated Au atom (not shown). In the first case, i.e., the Au₄H₂(2c)O₂(3c)⁺ complex, the binding energy of the adsorbed molecules to the gold cluster cation is 1.05 eV with the adsorption energy of O₂ calculated to be reduced to 0.43 eV. Here we find an additional slight reduction in bond activation (d(O−O) = 1.31 Å) and a corresponding smaller value of the estimator S(2π*) = 0.36. For the reaction paths leading to dissociation of the adsorbed oxygen molecule in the presence of preadsorbed hydrogen see our discussion below.

The dependence of the oxygen adsorption characteristics on the adsorption configuration is illustrated through consideration of the Au₄(H₂)₃(3c,3c,2c)O₂(2c)⁺ complex, shown in Figure 8c,d. Here the oxygen molecule is anchored to a 2-fold-coordinated Au atom (labeled 1 in Figure 8c), with only one of the O atoms bonded directly to the Au atom of the cluster (d(Au−O) = 2.14 Å), and the molecule forms an angle of 120° with respect to the plane of the Au₄⁺ cluster (see the side view in Figure 8c). Here the total binding energy of the adsorbed molecules is 2.19 eV (with reference to the ground state of the bare Au₄⁺ cluster), and the binding energy of the O₂ molecule to the cluster with three H₂ molecules preadsorbed to it (i.e., Au₄(H₂)₃(3c,3c,2c)⁺) is reduced to 0.52 eV, compared to oxygen adsorption at the 3-fold-coordinated Au atom discussed above.
The ground-state geometry of the parent neutral Au₆ cluster is an atom at the middle of the base of the triangle (see Figure 9). The distances between neighboring atoms along the edges (denoted by the solid dots (accompanied by illustrations of the corresponding atomic arrangements). The hydrogen-saturated structure Au₆(H₂)₃⁺ is shown in the inset. Au atoms are depicted by yellow balls, hydrogen atoms by blue balls, and oxygen atoms by red balls.

As in the case discussed above, where for the (H₂)₃(3c,2c,2c) configuration of the coadsorbed hydrogen molecules (see Figure 6b) we found that the excess charge (0.15e) in the Au₆(H₂)₃(3c,3c,2c)⁺ system is not distributed evenly among the Au atoms (see Figure 6b), here too the majority of the excess electronic charge on the gold cluster resides on the bare 2-fold-coordinated Au atom (0.1e) with the rest divided between the two 3-fold-coordinated Au atoms (labeled 2 and 3; see Figure 8b). In contrast to the case of O₂ adsorption on the 3-fold-coordinated Au atom (Figure 6c), in the present case, adsorption on the 2-fold-coordinated Au atom (labeled 1 in Figure 8c) involves only a small excess charge localization on the adsorbed molecule (0.03e), resulting in an essentially unactivated O₂ molecule (d(O–O) = 1.28 Å), as reflected also in a relatively small value of the antibonding population estimator $S(2\sigma^*) = 0.25$.

3.2.1.2. Au₆⁺ Cluster. In the ground state the atoms in the Au₆⁺ cluster are arranged in a triangular (t) structure (see the top row in Figure 9) with the average distance between neighboring atoms along the edges $d_{edge}(Au–Au) = 2.63$ Å, and the (internal) distances between neighboring atoms vary from 2.89 Å between the two midatoms on the sides of the triangle and 2.76 Å between a midatom on the side edge and an atom at the middle of the base of the triangle (see Figure 9). The ground-state geometry of the parent neutral Au₆ cluster is also triangular with a calculated vertical ionization potential vIP = 8.11 eV and an adiabatic ionization potential aIP = 8.08 eV.

The structure of the closest higher energy (0.19 eV) isomer of the hexamer cation cluster is an incomplete hexagon (see the top row in Figure 9), with $d_{edge}(Au–Au) = 2.73$ Å for the two upper Au–Au distances and $d_{edge}(Au–Au) = 2.65$ Å for the two lower ones, with the values for the side ones being $d_{edge}(Au–Au) = 2.66$ Å; the distance between the top and “middle” Au atoms is 2.77 Å. The transformation from the t to the ih structure involves an activation energy $\Delta E(t–ih) = 0.38$ eV, and the transition-state structure is nontriangular (see the top row in Figure 9).

At saturation the triangular hexamer cation cluster binds three H₂ molecules at the apexes of the triangle with a binding energy of $E_b(3H₂⁺) = 0.40$ eV per molecule, $d(H–H) = 0.80$ Å, $d(Au–H) = (1.91–1.96)$ Å (with the lower value corresponding to the top of the triangle); the average Au–Au distance after hydrogen adsorption is $d_{edge}(Au–Au) = 2.68$ Å (see Figure 9, middle row). This structure is essentially degenerate in energy with an incomplete hexagonal one with three H₂ molecules adsorbed to it (see Figure 9, middle row, right, where in the hydrogenated cluster the top H₂ molecule is in the plane of the gold atoms and the other H₂ molecules are normal to it). The transition between the triangular and the ih structure (with three H₂ adsorbed molecules) entails an activation barrier of 0.30 eV. In the hydrogenated triangular cluster we find an excess electronic charge on the Au atoms (see Figure 10b), with 0.076e on each of the bottom (base) Au apex atoms (labeled 4 and 6 in Figure 10c) and a charge deficiency of 0.04 on the top apex atom (labeled 1 in Figure 10c).

For the incomplete hexagonal structure at saturation the cluster cation binds five H₂ molecules at all the apex atoms, with an average binding energy per molecule of $E_b(5H₂⁺) = 0.38$ eV (see Figure 10a); in this cluster $d(Au–H) = 1.89$ Å and $d(H–H) = 0.81$ Å. In the hydrogenated cluster there is excess electronic charge on the gold atoms with a total of 0.06e on the apex atoms (distributed mainly on the atoms labeled 2, 3, 5, and 6 in Figure 10a) and 0.105e on the internal atom (labeled 1).
3.2.2. Reaction Paths. In this section we focus on interactions between molecular hydrogen and oxygen that, catalyzed by gold cluster cations, lead to reactions between them. In particular, we explore reaction pathways that lead to dissociation of the O₂ molecule and water elimination. The RP was calculated for the adsorption geometry Au₄(H₂)₃O₂(3c)²⁺, marked as configuration B (see also Figure 8c). One of the profiles leads to dissociation of the O₂ molecule and water elimination (the one passing through activation barrier F₂), while another one (the one passing through activation barrier F₁) does not lead to the desired product. The RP was calculated for the adsorption geometry Au₄(H₂)₃(3c,3c,2c)O₂(2c)²⁺, marked as configuration B (see also Figure 8c). The transition states encountered on the RP resulting in dissociation of the O₂ molecule correspond to the configurations marked D, F₁, and J, and the TS barriers are given in the figure. The hydrogen-saturated structure Au₄(H₂)₃⁺ is shown in the inset. Au atoms are depicted by yellow balls, hydrogen atoms by blue balls, and oxygen atoms by red balls.

4). The fully hydrogenated Au₄(ih)(H₂)₃⁻ cluster corresponds to the product stoichiometry Au₄H₆O₂ (mass peak labeled (6,10,0)) in the experimentally measured spectrum shown in Figure 4h.

Since in the experiment oxygen adsorption was found for a cluster with three coadsorbed hydrogen molecules (see the mass peak labeled (6,6,2) in Figure 4i), we explored the adsorption of O₂ to the saturated triangular cluster, as shown in Figure 9 (bottom row). The total binding energy of the adsorbed molecules is 1.63 eV, and the adsorption energy of the O₂ molecule is 0.42 eV. The adsorbed molecule is only slightly negatively charged (0.04e), and consequently, it is only weakly activated (d(O—O) = 1.28 Å); d(Au—O) = 2.18 Å. The Au₄(ih)(H₂)₂O₂⁺ cluster may transform to a higher energy isomer (0.14 eV) with an ih structure via an activation barrier of 0.28 eV (see the bottom row in Figure 9). Instead it may transform, via a transition-state barrier of 0.38 eV, to a lower energy (0.72 eV) of ih geometry (containing a hydroperoxo group), as discussed in the context of the reaction path described in Figure 14 (transition from B₃ to D).

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3.2.2. Reaction Paths. In this section we focus on interactions between molecular hydrogen and oxygen that, catalyzed by gold cluster cations, lead to reactions between them. In particular, we explore reaction pathways that lead to dissociation of the O₂ molecule, starting from coadsorbed molecular hydrogen and oxygen (i.e., following a Langmuir—Hinshelwood mechanism, discussed for the reaction catalyzed by the gold tetramer and hexamer cations), as well as a case where the reaction proceeds through the interaction of preadsorbed molecular hydrogen with a gaseous oxygen molecule (that is, an Eley—Rideal mechanism, discussed as an alternative mechanism of the reaction catalyzed by the gold hexamer cation). In both cases we find that the reaction pathway involves formation of a complex containing a hydroperoxo group as a reaction intermediate. To facilitate our discussion, we present RPs, where
2-fold- and 3-fold-coordinated Au atoms) we find a well-bound O2 molecule (with adsorption of the molecule being barrier free) that is activated close to a superooxo state when bound to a 3-fold-coordinated Au atom (bond length \(d(O-O; \text{Au}_4(H_2)O_2(3c)^+) = 1.33 \text{ Å} \) in Figures 6c and 11, configuration B). When the trap is heated to 200 K, \(\text{Au}_4H_4^+\) is detected instead of the saturation hydrogen coverage \(\text{Au}_4H_4^+\) (see trace d in Figure 4); the calculated total energy difference between the ground-state energies of \(\text{Au}_4H_4^+\) and \(\text{Au}_4H_4^+\) ranges between 1.28 and 0.95 eV, depending on the H2 adsorption sites (see Table 1).

Only when the temperature is increased to 300 K do we observe new products. Indeed, at this temperature one observes in addition to the bare \(\text{Au}_4^+\) signal a new mass peak corresponding to the mass of \(\text{Au}_4H_2O_4^+\) containing a single oxygen atom, with the mass peak corresponding to \(\text{Au}_4H_2O_2^+\) disappearing, reflecting the dissociation of the initially coadsorbed O2 molecule. Reaction profiles, starting from the two adsorption geometries of the O2 molecule, are shown in Figures 11 and 12, with an additional RP, corresponding to O2 adsorption at the Au(3c) site (as in Figure 11), but with only a single coadsorbed H2 molecule, displayed in Figure 13 (this case has not been observed experimentally). The calculated reaction profiles in Figures 11–13 reveal the microscopic mechanism of the reaction starting from the ground state of \(\text{Au}_4H_2O_2^+\) (B). In Figure 11 a TS energy barrier (\(\Delta E_t = 0.34 \text{ eV}\)) is encountered in taking the system from configuration B to the TS configuration (C, where \(d(O-O) = 1.28 \text{ Å}\)), which relaxes to the hydroperoxo (−OOH) configuration marked D in Figure 11 (in this configuration \(d(O-O) = 1.41 \text{ Å}\) and \(d(O-H) = 0.99 \text{ Å}\)). Traversing a subsequent small TS barrier (\(\Delta E_b = 0.08 \text{ eV}\)), the system relaxes to a configuration G with a weakly adsorbed H2O molecule, whose removal entails an energy of 0.40 eV, resulting in \(\text{Au}_4H_4O^+\). Removal of the H2 molecule (bonded to the left corner of the gold triangle in G) requires an additional 0.61 eV, thus obtaining \(\text{Au}_4H_3O^+\), which can be identified with the mass peak labeled (4,2,1) in the experimentally measured mass spectrum (Figure 4f).

Starting from configuration B in Figure 12, corresponding to a slightly activated coadsorbed oxygen molecule anchored to a gold cluster cation at a Au(2c) site, formation of the hydroperoxo intermediate (configuration E in Figure 12) requires a larger TS barrier, \(\Delta E_d = 0.44 \text{ eV}\). An even larger TS barrier, \(\Delta E_{bd} = 0.65 \text{ eV}\), is encountered toward the eventual formation of an adsorbed water molecule and a single adsorbed oxygen atom (configuration K in Figure 12). The energy required for the water molecule elimination is 0.63 eV, and an additional 0.46 eV is required for desorption of the (bottom) H2 molecule, resulting in formation of the aforementioned \(\text{Au}_4H_3O^+\) product; the energy liberated in the transition from G to H is sufficient for the desorption of both the H2O and H2 molecules. We also included in Figure 12 a reaction path that does not lead to formation of an adsorbed water molecule and does not yield the desired product (see the path E → Fb → Gb, involving a barrier \(\Delta E_{rb} = 0.36 \text{ eV}\)).

To illustrate the dependence of the RP of the oxygen molecule on the hydrogen coverage, we display in Figure 13 the RP for a single coadsorbed H2 molecule, starting from configuration B (\(E_b(O_2) = 0.50 \text{ eV}, d(O-O) = 1.32 \text{ Å}\)) of the \(\text{Au}_4H_2(2c)O_2(3c)^+\) cluster. Here we encounter a succession of two TS barriers, \(\Delta E_{bc} = 0.17 \text{ eV}\) and \(\Delta E_{cd} = 0.20 \text{ eV}\) (or in a combined form \(\Delta E_{bd} = 0.37 \text{ eV}\)) with \(d(Au-O) = 2.22 \text{ Å}, d(O-O) = 1.28 \text{ Å}, \) and \(d(O-H) = 2.475 \text{ Å}\) at TS configuration D. Relaxation from the TS leads to formation of a hydroperoxo intermediate E, with \(d(O-O) = 1.36 \text{ Å}\) and \(d(O-H) = 1.03 \text{ Å}\). The hydroperoxo group transforms through a higher activation barrier (\(\Delta E_{t} = 0.46 \text{ eV}\)) to a \(\text{H}_2O-\text{O}^-\) intermediate G, which leads to formation of an adsorbed water molecule and an adsorbed single oxygen atom (configuration I) through an additional TS barrier \(\Delta E_{gi} = 0.23 \text{ eV}\). Removal of the adsorbed \(\text{H}_2O\) molecule requires an energy of 0.735 eV (which is readily available from the energy liberated in the transition from H to I). Altogether, the prohibitive complexity of the reaction mechanism and the relatively large multiple activation energy barriers encountered in the reaction involving a single coadsorbed \(\text{H}_2\) molecule (Figure 13), in comparison with the relatively simple and facile reaction profile corresponding to the reaction of adsorbed \(\text{O}_2\) in the presence of three coadsorbed \(\text{H}_2\) molecules as displayed in Figure 11, serve to illustrate the promoting effect of the increased coverage of coadsorbed hydrogen on the dissociation reaction of an adsorbed oxygen molecule on gold tetramer cation clusters (Figure 11).

### 3.2.2.2. Reactions on \(\text{Au}_6^+\)

When the gold hexamer cation interacts at 100 K with hydrogen only, a saturated species with five \(\text{H}_2\) molecules per cluster is observed (see mass peak labeled (6,10,0) in Figure 4h corresponding to an incomplete hexagonal structure of \(\text{Au}_6(\text{H}_2)^5\), shown in Figure 10a and in the inset of Figure 14). However, when both \(\text{O}_2\) and \(\text{H}_2\) are admitted to the trap at 100 K, the coadsorption product labeled (6,6,2) in the mass spectrum shown in Figure 4i, corresponding to the triangular structure of \(\text{Au}_6d(\text{O}(\text{H})_2)\), is the sole mass signal found (cf. the bottom row of Figure 9, Figure 10c, and configuration B in Figure 14), where the total binding energy of the three \(\text{H}_2\) molecules is 1.21 eV and that of the coadsorbed \(\text{O}_2\) molecule is 0.42 eV. As aforementioned, the activation and dissociation of the coadsorbed oxygen molecule with increasing temperature is even more apparent for the \(\text{Au}_6^+\) cluster than for the gold tetramer cation discussed above. Indeed, trace k in Figure 4, obtained at an increased reaction time of 2.0 s and 200 K, reveals that already at this relatively low temperature an additional mass peak corresponding to a dissociated oxygen species (labeled (6,4,1)) emerges (while for the gold tetramer oxygen dissociation required heating to 300 K; see Figure 4f).

The RP, starting from the coadsorption ground-state configuration B in Figure 14, exhibiting a Langmuir–Hinselwood mechanism. We find that the triangular-shaped ground-state gold cluster cation transforms to an incomplete hexagonal geometry with a hydroperoxo group (see D in Figure 14) through a TS activation barrier \(\Delta E_{C} = 0.38 \text{ eV}\); in the TS configuration \(C_b\), \(d(O-O) = 1.30 \text{ Å}\) and the distance between the closest O and H atoms is \(d(O-H) = 1.40 \text{ Å}\). The gain in energy in transforming from the TS to the hydroperoxo intermediate (configuration D) is 0.72 eV, and in D \(d(O-O) = 1.37 \text{ Å}\) and \(d(O-H) = 1.03 \text{ Å}\). The energy required to remove one of the bottom hydrogen molecules from configuration D is 0.53 eV, leaving a cluster with a nuclearity of \(\text{Au}_6(\text{H}_2)^3\) corresponding to the mass peak labeled (6,4,2) in the experimental spectra shown in Figure 4j,k.

Subsequently, we find two TS barriers: one for rotation of the hydroperoxo group (configuration F) with a barrier \(\Delta E_{t} = 0.24 \text{ eV}\) and the other for forming the complex marked H which entails a barrier of \(\Delta E_{i} = 0.46 \text{ eV}\). Subsequent relaxation leads to water elimination ending with \(\text{Au}_6H_3O^+\) (configuration I) containing a dissociated, single, adsorbed oxygen atom. This final configuration corresponds to the mass peak labeled (6,4,1) in the measured mass spectra in Figure 4k,l. We note that, in
agreement with the experiments, the O₂ dissociation reaction for the Au₆⁺ cluster is predicted to entail smaller activation barriers than in the Au₄⁺ case, and is thus expected to occur at a lower temperature, as is indeed observed; as aforementioned, Au₄H₃O⁺ products are detected already at 200 K for Au₆⁺, but only at 300 K for Au₄⁺.

Up to this point all the reaction mechanisms that we discussed were of the Langmuir−Hinshelwood (LH) type, starting from reactants (hydrogen and oxygen molecules) coadsorbed on the gold cluster cation. We close with a discussion of an alternative reaction mechanism for the reaction on the gold hexamer cation, which is of the Eley−Rideal (ER) type, indicated by the path \( \Lambda \rightarrow B \rightarrow C \rightarrow D \rightarrow \ldots \) in Figure 14. In this mechanism we start from the hydrogen-saturated triangular structure of the Au₆(H₂)₃⁺ cluster (Bu, with the total binding energy of the H₂ molecules being 1.21 eV). A gaseous O₂ molecule binds to the cluster through a TS barrier \( \Delta E_{\text{t}} = 0.28 \) eV; see the TS configuration labeled C_\text{t}, where the inter-hydrogen atom distance in the molecule involved in the reaction \( d(\text{H}−\text{H}) = 0.96 \) Å, \( d(\text{O}−\text{O}) = 1.28 \) Å, and \( d(\text{O}−\text{H}) = 1.35 \) Å. Relaxation from the TS transforms the gold cluster to an incomplete hexagonal structure and results in formation of a hydperoxo intermediate (configuration D, discussed above for the LH mechanism). Subsequent steps of the reaction leading to oxygen dissociation and water elimination are the same as those discussed above for the LH mechanism.

4. Summary

In this paper we presented a joint experimental and theoretical study where we have explored the characteristics and factors that control the cooperative coadsorption of hydrogen and oxygen on cationic gold clusters Au_x⁺ (x = 2−7), with a particular emphasis on Au₄⁺ and Au₆⁺. Product ion mass distributions were obtained in an octopole ion trap under multicollosion conditions at temperatures of 300, 200, and 100 K as well as for ion storage times \( t_k = 0.1−2 \) s. The temperature-dependent reactions of the clusters exposed to solely hydrogen revealed a strictly negative temperature dependence and thus a barrier-free hydrogen chemisorption with saturation coverages of H₂ molecules corresponding to the number of corner sites in the ground-state structures of the clusters (except for Au₅⁺ where the hydrogen saturation coverage of three H₂ exceeds the number of corners; see Figure 2). In contrast, temperature-dependent measurements for Au₄⁺ and Au₆⁺ yield a negative temperature dependence for Au₄H₂O₀⁺ products, but a positive temperature dependence for Au₅H₃O⁺, indicating the presence of an activation barrier in the latter case.

First-principles calculations, based on density-functional theory, provided a detailed picture of the nature of the adsorption of H₂ and O₂ to cationic gold clusters. Bonding of H₂ molecules to the cluster cations was found to involve the transfer of charge from the molecules to the gold atoms. The calculated saturation coverages agree with the experimental ones (four H₂ molecules and five H₂ molecules for Au₄⁺ and Au₆⁺, respectively; see Figures 2, 4, 6, 8, and 10). For the case of Au₆⁺, the ground-state structure was determined to have a triangular atomic arrangement and a higher energy isomer (0.19 eV) with an incomplete hexagonal (ih) structure was found (Figure 9). At saturation coverage of the triangular structure (that is, the adsorption of three H₂ molecules) the triangular and ih isomer (Au₆(ih)(H₂)₃⁺) are found to become degenerate in energy, and the transformation between these structures upon adsorption (termed also “structural fluctionality”) was determined to involve a barrier of 0.30 eV (see Figure 9); a similar barrier separates the two isomers with coadsorbed three H₂ molecules and one O₂ molecule (see the bottom row of Figure 9).

The coadsorption of O₂ was found to entail occupation of the antibonding \( 2\pi^* \) orbitals of the molecule (see the analysis in Figure 7), resulting in excess electronic charge accumulation on the adsorbed molecule (see Figures 6, 8, and 10), with a consequent weakening of the O−O bond, and activation of the adsorbed molecule.

Theoretical investigations of the evolution of the reaction along the reaction coordinate allowed elucidation of the dynamics and microscopic mechanisms and determination of reaction profiles and activation barriers. The measurements (see Figure 4) and the theoretical analysis (see Figures 11−14) revealed that the promotion and activation of molecular oxygen by hydrogen preadsorption leads to the formation of a hydroperoxo intermediate on Au₄⁺ and Au₆⁺, culminating with the dissociation of O₂ via the release of H₂O. Langmuir−Hinshelwood reaction mechanisms involving the coadsorption of both of the reactant molecules were discussed for both cluster sizes (Figures 11−14), and an alternative Eley−Rideal mechanism involving hydrogen molecules adsorbed on a Au₆⁺ cluster reacting with an impinging gaseous oxygen molecule (see Figure 14) was analyzed.

The theoretical results for saturation coverages and reaciton characteristics were found to agree with the experimental findings. The joint investigations provide useful insights regarding hydrogen and oxygen cooperative adsorption effects and consequent reaction mechanisms. In particular, the current findings guide our ongoing analysis pertaining to selective hydrocarbon oxidation by molecular oxygen on free and supported gold particles, in which hydrogen preadsorption is found to be required to achieve an efficient and highly selective process.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. S.M.L. thanks the Fonds der Chemischen Industrie in particular for a Kekulé fellowship. The theoretical work (R.N.B., B.Y., and U.L.) was supported by the U.S. Department of Energy, the Air Force Office for Scientific Research, and the NSF. Calculations were performed at NERSC, Berkeley, CA, the DOD supercomputer center, and the Georgia Tech Center for Computational Materials Science.

JA9022368