

Reactivity of Atomic Gold Anions toward Oxygen and the Oxidation of CO: Experiment and Theory

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Abstract: Results for the binding of carbon monoxide and oxygen along with the oxidation of CO in the presence of atomic Au⁻ have been obtained utilizing a fast-flow reactor mass spectrometer. In addition, density functional calculations have been performed to explain the experimental findings. It was observed that upon oxygen addition to the metal plasma, gold oxide species of the form AuO_n⁻, where $n = 1-3$, were produced. The addition of carbon monoxide to the preoxidized gold atom revealed that AuO⁻ and AuO₃⁻ promote the oxidation of CO. Density functional calculations on structures and their energetics confirmed the experimental findings and allowed us to propose mechanisms for the oxidation of carbon monoxide. The reactions of CO with AuO_{1,3}⁻ proceed via complex formation with CO bound to the oxygen atom, followed by either cleavage of the Au–O bond or complex rearrangement to form a weakly bound CO₂ unit, leading in both cases to the emanation of CO₂.

Introduction

Laying the foundation for developing catalysts that can influence the selectivity and efficiency of desired reaction channels comprises a major research activity of considerable current interest. Particularly promising in this context are nanoscale catalysts whose composition may be tailored to acquire the desired chemical properties. Studies of clusters are providing new insights into the prospects of accomplishing this goal. Indeed, a study of their reactivity can be especially valuable in catalyst development through elucidating the influence which various stoichiometries and oxidation states have on reaction mechanisms. One especially active area comprises efforts to affect the abatement of pollutants such as the oxidation of carbon monoxide to CO₂. Oxidation of this toxic gas is of importance for many practical applications beyond combustion exhausts, including the development of CO detection devices and improved efficiency of CO₂ lasers.¹

In searches for suitable catalysts to perform and possibly enhance this oxidation process, gold has come under intense scrutiny. Although bulk gold has long been thought to be catalytically inactive, recent findings suggest that nanosized gold particles supported on metal oxides provide an enhanced pathway of CO removal by oxidation.^{1,2} For example, Haruta and co-workers have found that, when deposited onto select metal oxides, ultra-fine gold particles exhibit high activities for the oxidation of carbon monoxide.³ Furthermore, they deter-

mined that the catalytic activity depends on the preparation method as well as both the support and the particle size.^{1,4}

Supported gold catalysts have received much attention in the recent past. However, the mechanisms and processes responsible for the size dependent interactions are not well understood. It has been proposed that the charge state⁵ and a charge transfer from the support to the adsorbate play a crucial role in the activity⁶ of supported gold particles. Gas-phase gold clusters provide valuable model systems for investigating interactions taking place on catalytic surfaces,⁷ thereby providing complementary information that serves to unravel the mechanisms involved. Ensembles of atoms on catalytic surfaces have been described as “cluster-like”,⁸ and due to the similarity between their electronic structures⁹ and those of free anionic gold clusters, it has been realized that a study of the reactions of free gold cluster anions can provide information useful in elucidating the role of degree of aggregation, charge state, and stoichiometry on mechanisms involved in the catalytic oxidation of carbon monoxide by gold.

Despite many recent valuable experimental and theoretical contributions, the question remains whether molecular or dissociative oxygen is formed on gold clusters providing the

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mechanism for the reaction and removal of CO by oxidation. The present paper presents results obtained by a joint experimental and theoretical effort for the binding of oxygen to the atomic gold anion and the oxidation of carbon monoxide on the monomer. Our experimental conditions differ with respect to prior experiments reported in the literature. In particular, it is important to note that the preparation technique employed for the studies reported herein and described later enabled the facile dissociation of oxygen molecules, and hence, the acquisition of thermodynamically stable structures of gold–oxygen complexes that are inaccessible through direct interactions of oxygen molecules with gold cluster anions. Hence, in contrast to the work of others, our studies focus on the reactions arising from gold species with bound oxygen atoms, specifically the oxidized atomic gold anion in this first paper of a series. Our theoretical findings provide a different perspective on the potential reaction mechanisms for the energetically most favorable complexes of oxygen bound to gold anions and their selective reactivity toward the CO molecule. The mechanism found is of general validity and, in connection with quantitative kinetic considerations, is able to account for the observed reactivity patterns of the studied AuO_n^- ($n = 1, 3$) clusters.

This paper provides a survey of previous findings on the reactivity of gold anionic clusters with O_2 , followed by a brief overview of experimental and theoretical techniques. Thereafter, the results and discussion of the new findings are presented.

Previous Investigations of Gold Cluster Anions and Reactivity toward O_2 and CO. The behavior of gold cluster anions has been studied rather extensively in the gas phase.^{2,9–13} As surveyed in what follows, particular focus had been given to establishing an understanding of the binding patterns of molecular oxygen to the clusters and reactions of the cluster anion complexes with CO .^{2,9–12}

In one detailed study, Lee and Ervin performed low-pressure guided-ion beam studies on Au_n^- ($n = 2–7$) in order to obtain relative reactivities. They found extremely slow depletion rates near their detection limits for the odd- n clusters Au_n^- ($n = 1–7$) and observed products for reactions between molecular oxygen and Au_n^- ($n = 2–7$) having even values of n only.¹⁰ Cox and co-workers have examined the reactivity and saturation of small gold clusters, also finding that only the anions with an even number of atoms are reactive with O_2 .⁵ They account for this behavior in terms of being similar to the electron affinity variation with cluster size and propose that the electronic nature of both the cluster and the adsorbate affect the dissociative chemisorption of oxygen onto gold clusters.⁵ In related type studies, Wallace and Whetten, employing pulsed-helium flow techniques, report that either no, or at most one O_2 adsorbs intact onto most even n Au_n^- for $n = 2–22$, but they do not observe any secondary adsorptive uptake of O_2 .¹⁴ They also relate the patterns of reactivity with the electron affinities.¹⁴ It is known from the early work of Smalley and co-workers that clusters of the coinage metals (<30 atoms) exhibit an even–odd alternation in the values of the electron affinities.¹⁵ This behavior was

qualitatively explained in terms of filling the spherical electron shells and spheroidal subshells by valence electrons.¹⁵ The correlation between electron affinities and the shell model concept is poor for small clusters since the structural properties play an important role. Wallace and Whetten's explanation for the lack of reactivity of odd n Au_n^- is that if the di-oxygen acts as a one-electron acceptor, the anionic species will be left with an unpaired electron yielding a high electron affinity.¹⁴ They also attribute the lack of secondary O_2 adsorption to this explanation.¹⁴

It should be noted that most reports in the literature for the binding of oxygen to Au_n^- do not include any results for the atomic gold anion,^{5,14} and in the case of Lee and Ervin, slow depletion rates for Au_n^- ($n = 1–7$) with odd n were reported.¹⁰ Only Ganteför, Jena and co-workers report findings in which Au^- and Au_3^- are the only odd- n Au_n^- species observed to react with O_2 to some extent.^{9,16} They have found that the ground-state structure for the AuO_2^- complex is a linear chain with dissociated oxygen atoms.

The oxidation of carbon monoxide has been studied both experimentally and theoretically by Heiz and Landman and co-workers.² With temperature-programmed reaction studies, they were able to examine the combustion of carbon monoxide on supported, size-selected gold clusters Au_x for x up to 20.² From these studies, it follows that the oxidation of CO is size-dependent in nature with Au_8 being the smallest size cluster to catalyze the reaction. Furthermore, their DFT calculations reveal that the cluster is charged by a partial electron transfer from the oxide support.² Heiz, Landman, and co-workers report that these factors, as well as the presence of F-center defects, play an important part in the activation of gold as a catalyst.² However, they did not observe any activity for species smaller than the octamer.² Therefore, their main focus was to ascertain the reason for this activity. From these studies, it was found that CO desorbs from the supported Au_8 cluster in the absence of oxygen.² Furthermore, they propose that the dissociation of the oxygen in the presence of the CO molecule is responsible for the formation of the CO_2 .

Wallace and Whetten found cooperative coadsorption to occur with CO and molecular oxygen on gas-phase gold cluster anions.¹¹ This suggests that the presence of one of the adsorbates on the cluster assists in the adsorption of the other species. In fact, they observe that a species that does not typically adsorb CO, namely Au_2^- , will bind the molecule when molecular oxygen is already present on the cluster.¹¹ They report that the same product composition is produced when the reactant gas is added at the source as when it is introduced following cluster formation. From these experimental studies, which take place under reaction saturation conditions and involve the adsorption of oxygen molecules in the superoxo form¹¹ as opposed to oxygen atoms, they find the highest rate of CO oxidation for Au_6^- .

Wallace and Whetten also propose a reaction cycle in which the formation of CO_2 depends on the appearance of peaks that correspond to $\text{Au}_n\text{CO}_m\text{O}^-$.¹¹ The reaction mechanism involves the dissociation of the O_2 molecule for the oxidation of CO. Along with the appearance of $\text{Au}_n\text{CO}_m\text{O}^-$ peaks, they also

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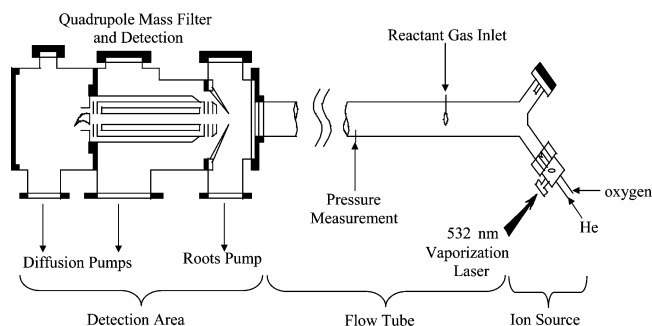


Figure 1. Metal ion fast flow reactor apparatus for experimental investigation.

observe the recovery of $\text{Au}_n(\text{CO})_{m-1}^-$ peaks.¹¹ Furthermore, Wöste and co-workers have produced $\text{Au}_n(\text{CO})_m(\text{O}_2)_x^-$ species through the reactions of carbon monoxide and oxygen with mass-selected gold cluster anions.¹² Their results show that the reactivity with CO and O_2 depends on the cluster size and charge state.¹² Moreover, they find that the appearance of the $\text{Au}_n(\text{CO})_m(\text{O}_2)_x^-$ clusters has a temperature dependent behavior, appearing only at temperatures near 100 K.¹²

It is interesting to note that work by Kim et al. has shown that utilizing a rf-plasma jet source, oxygen atoms can be produced and adsorbed onto a Au/TiO₂-(110) planar model catalyst.¹⁷ Under ultrahigh vacuum conditions, the introduction of gas-phase CO molecules onto this cryogenically cooled surface produces CO₂.¹⁷ Furthermore, Kim and co-workers found little change in the CO₂ production with cluster size as reported by Valden et al.¹⁸ To our knowledge, no reaction of gas-phase atomic gold anions toward oxygen and CO has been reported until now.

Experimental and Computational Methods and Accuracy.

In the present study, a fast flow reactor mass spectrometer coupled to a laser vaporization source, which has been described in detail previously,^{19,20} is used to investigate the interactions of carbon monoxide and oxygen on gold cluster anions. A schematic of this apparatus is shown in Figure 1. Briefly, gold oxide clusters are produced in a laser vaporization source by passing a continuous flow of oxygen seeded in helium over the metal plasma formed by ablating a rotating and translating gold rod with the second harmonic of a Nd:YAG laser. The formed clusters exit the source region through a conical nozzle into the flow tube where the reactant gas, carbon monoxide in this case, is introduced in varying amounts downstream at a reactant gas inlet. Once formed, most of the reaction products and the helium buffer gas are pumped away by a high volume roots pump. Those species that are not pumped off are sampled through a 1 mm orifice and focused by a set of electrostatic lenses into the quadrupole mass analyzer. The products are subsequently detected utilizing a channel electron multiplier.

Structural calculations presented in this contribution have been performed using DFT method with Becke's hybrid three parameter nonlocal exchange functional together with the Lee–Yang–Parr gradient corrected correlation functional (B3LYP).^{21,22,23} In order to take into account the relativistic effects which have

a substantial influence on the bonding properties involving gold atoms, we used the 19-electron relativistic effective core potential (19-RECP) from the Stuttgart group and the [8s7p5d1f]/[7s5p3d1f] AO basis set.^{24,25} For the oxygen atom, the 6–311 G(d) triple-split valence basis set has been employed. Our previous work on the adsorption of molecular oxygen on hydrated gold clusters has shown that this method provides the appropriate accuracy needed for proper description of the gold–oxygen interaction.²⁶ In addition, in order to test the ability of the method to describe the bonding of gold with oxygen atoms, benchmark CCSD(T) calculations were performed on the AuO[−] system. Because the CCSD(T) method requires use of larger basis sets in order to obtain very reliable results, a [9s9p6d4f] AO basis set for gold was used, and the AO basis for oxygen^{27,28} has been augmented with an additional diffuse function. The calculated dissociation energy of AuO[−] into the thermodynamically most stable products is 1.72 eV which compares well with the DFT value of 1.94 eV. In both DFT and CCSD(T) methods, the ground electronic state of AuO[−] is a singlet state with an energy separation from the triplet state of 0.230 and 0.39 eV, respectively. All structures presented in this work have been fully optimized using gradient minimization techniques and have been characterized by the frequency analysis. The reaction mechanism has been studied by performing ab initio MD using forces calculated with both the B3LYP and the RI (resolution of identity)-DFT procedure. This enabled us to study the reaction mechanisms in greater detail and to obtain basic information on the time scales of the processes involved as well as the energy dependence of the studied reaction channels.

Results

Reactions of Bare Atomic Gold Anions with Oxygen. The interaction of gold cluster anions with oxygen has been investigated using a fast flow reactor and employing density functional method. The results provide new insights into the reactive species of gold–oxygen anion complexes possessing one gold atom, and also reveal the possible reaction mechanisms involved.

The binding of oxygen to the gold cluster anions, with the oxygen being in both molecular and atomized forms, was investigated in the present study by seeding the oxygen in helium and passing this mixture over the ablated metal surface of the rod, producing the preoxidized gold cluster anions. This spectrum, presented in Figure 2, shows that Au[−], Au₂[−], and Au₃[−] will bind oxygen under the present experimental conditions.

The Au[−] species binds up to three oxygen atoms, while the dimer and trimer (to be discussed in a subsequent paper) take up four and five oxygen atoms, respectively. In order to explain the observed abundances of the AuO_n[−] ($n = 1, 5$) species in the mass spectra obtained under thermalized conditions, the struc-

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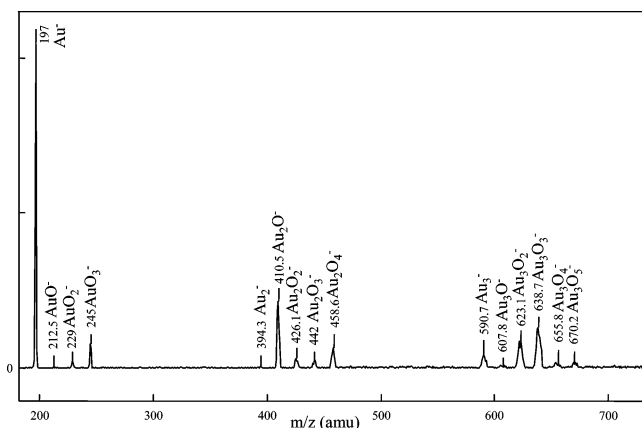


Figure 2. Mass spectrum for the adsorption of oxygen onto gold cluster anions.

tural properties and energetics of these clusters have been determined employing the DFT approach described above. The results are summarized in Figure 3 and Table 1.

The ground state of AuO^- has been calculated to be a singlet state with the equilibrium bond length of 1.882 Å. The triplet state is higher in energy by 0.230 eV and has a weakened bond which is reflected in a larger Au–O distance of 2.046 Å. The dissociation energy leading to singlet Au^- and singlet oxygen atom has a value of 4.72 eV. However, due to the crossing between the singlet ground state and the close lying triplet state, the lowest energy dissociation channel for AuO^- is actually the one leading to singlet Au^- and triplet oxygen atom in the more stable triplet state requiring 1.94 eV (cf. Figure 3a).

The most stable structure of AuO_2^- is linear with oxygen atoms bound in the dissociated form and with the triplet ground state similar to that reported by Ganteför¹⁶ and Jena.⁹ The Au–O bond length of 1.849 Å is slightly shorter than in the case of AuO^- . The structure where the oxygen is molecularly adsorbed on the gold atom (isomer II) is 0.714 eV higher in energy. Corresponding structures in singlet states (isomers III and IV) are 1.068 and 1.495 eV higher in energy, respectively (cf. Figure 3a).

The energy required to break the Au–O bond in AuO_2^- , forming AuO^- in the most stable singlet state and an oxygen atom in the triplet state, is 4.22 eV. Although the most stable structure has oxygen adsorbed in the dissociated form, molecular dynamics simulations show that the dissociation of molecular oxygen on Au^- does not occur at thermal conditions. Therefore, it is expected that, due to the large barrier involved, the most stable structure can be formed under experimental conditions where the O_2 molecule is already dissociated, whereas in experiments performed using molecular oxygen, the less stable structure with oxygen adsorbed molecularly is expected to be the species present.

The most stable isomer of AuO_3^- (isomer I) has a triplet ground state and molecular oxygen adsorbed onto AuO^- . As can be seen from Figure 3a molecular oxygen on Au^- is bound in an activated form with the O–O bond length of 1.331 Å, corresponding to the superoxo form. The corresponding structure in the singlet state (isomer II) is 0.825 eV higher in energy. Two other structures (isomers III and IV) have an ozone O_3 unit bound to the Au^- , and they are 1.394 and 1.561 eV higher in energy, respectively. The most stable structure has two possible fragmentation channels, one leading to the dissociation

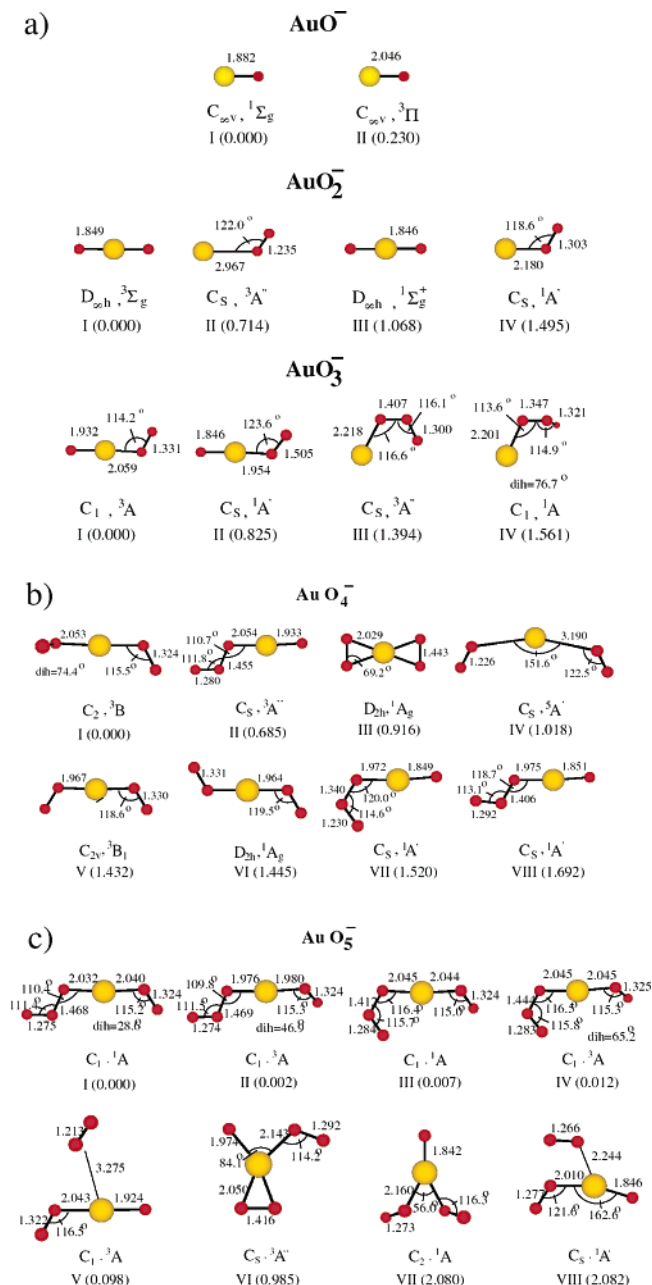


Figure 3. Predicted structures for AuO_n^- ($n = 1-5$). The energy differences in eV with respect to the most stable structure are given in round brackets. I–VIII label the energy sequence of the isomers. Labels of the symmetry group and the ground electronic state are also given. Bond distances are in Å.

of the oxygen atom bound to gold, requiring 2.60 eV, and the other leading to the fragmentation of O_2 , requiring 1.55 eV of energy.

In the lowest energy structure of AuO_4^- (isomer I), which has a triplet ground electronic state, two oxygen molecules are molecularly adsorbed on the Au^- atom. (cf. Figure 3b) The most favorable fragmentation channel accessible to AuO_4^- is the fragmentation of one O_2 subunit which requires only 0.427 eV of energy. The next structure higher in energy is the one with an oxygen atom and an O_3 subunit bound separately to the Au^- and is 0.685 eV higher in energy. All other structures shown in Figure 3b are significantly higher in energy and represent different spin states and different conformations of the two lowest energy isomers.

Table 1. Ground State Energies and Properties of AuO_n^- ($n = 1-5$) Clusters Obtained with the B3LYP Method

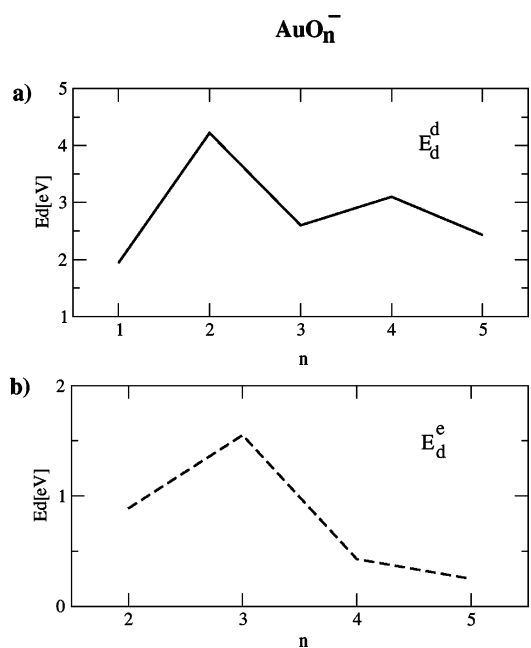
AuO_n^-	symm. (state)	energy a.u.	E_{rel}^a eV	E_b^b eV	E_c^c eV	E_d^d eV	E_e^e eV	NBO charge Au
AuO_1^-	$C_{\infty v} (^1\Sigma_g^-)$	-210.993018		2.00	0.97	1.94		-0.10
AuO_1^-	$C_{\infty v} (^3\Pi)$	-210.984576	0.230	1.89	0.78			
AuO_2^-	$D_{\infty h} (^3\Sigma_g^-)$	-286.233588		2.74	2.06	4.22	0.887	0.57
AuO_2^-	$C_s (^3A'')$	-286.207355	0.714	2.50	1.82			
AuO_2^-	$D_{\infty v} (\Sigma^{1+})$	-286.194338	1.068	2.39	1.70			
AuO_2^-	$C_s (^1A')$	-286.178640	1.495	2.24	1.56			
AuO_3^-	$C_1 (^3A)$	-361.414796		2.71	2.19	2.60	1.55	0.41
AuO_3^-	$C_s (^1A')$	-361.384480	0.825	2.50	1.99			
AuO_3^-	$C_s (^3A'')$	-361.363555	1.394	2.36	1.85			
AuO_3^-	$C_1 (^1A)$	-361.357434	1.561	2.32	1.80			
AuO_4^-	$C_2 (^3B)$	-436.614086		2.79	2.37	3.10	0.427	0.35
AuO_4^-	$C_s (^3A'')$	-436.588925	0.685	2.65	2.23			
AuO_4^-	$D_{2h} (^1A_g)$	-436.580418	0.916	2.61	2.19			
AuO_4^-	$C_s (^5A')$	-436.576683	1.018	2.59	2.17			
AuO_4^-	$C_{2v} (^3B_1)$	-436.561449	1.432	2.50	2.08			
AuO_4^-	$D_{2h} (^1A_g)$	-436.560973	1.445	2.50	2.08			
AuO_4^-	$C_s (^1A')$	-436.558233	1.520	2.49	2.07			
AuO_4^-	$C_s (^1A')$	-436.551902	1.692	2.45	2.03			
AuO_5^-	$C_1 (^1A)$	-511.788729		2.72	2.38	2.43	0.249	
AuO_5^-	$C_1 (^3A)$	-511.788655	0.002	2.72	2.38			
AuO_5^-	$C_1 (^1A)$	-511.788461	0.007	2.72	2.38			
AuO_5^-	$C_1 (^3A)$	-511.788291	0.012	2.72	2.38			
AuO_5^-	$C_1 (^3A)$	-511.785135	0.098	2.70	2.36			
AuO_5^-	$C_s (^3A'')$	-511.752525	0.985	2.56	2.37			
AuO_5^-	$C_2 (^1A)$	-511.712286	2.080	2.37	2.37			
AuO_5^-	$C_s (^1A')$	-511.712233	2.082	2.37	2.37			

^a Energy difference with respect to the most stable structure. ^b Binding energy per atom for the AuO_n^- complexes defined by $E_b = [E(\text{AuO}_n^-) - E(\text{Au}) - E(\text{O}^-) - (n-1)E(\text{O})]/(1-n)$. ^c Binding energy per atom for the AuO_n^- complexes defined by $E_b = [E(\text{AuO}_n^-) - E(\text{Au}^-) - nE(\text{O})]/(1+n)$. ^d Dissociation energy for the fragmentation of O atom ($\text{AuO}_n^- \rightarrow \text{AuO}_{n-1}^- + \text{O}$) calculated for the most stable products regardless of spin. ^e Dissociation energy for the fragmentation of the O_2 molecule ($\text{AuO}_n^- \rightarrow \text{AuO}_{n-2}^- + \text{O}_2$).

For AuO_5^- , five structures within 0.1 eV have been calculated as shown in Figure 3c. The lowest energy structure (isomer I) is a singlet with O_3 and O_2 subunits bound to the Au^- . The corresponding triplet structure (isomer II) is only 0.002 eV higher in energy. Isomers III and IV can be viewed upon as cis forms of isomers I and II and are 0.007 and 0.012 eV higher in energy, respectively. The fifth isomer is basically a AuO_3 with the oxygen molecule very weakly bound to the Au^- . All other structures found, which are shown in Figure 3c, are more than 1 eV higher in energy.

The lowest fragmentation channel for AuO_5^- is the fragmentation of the O_2 molecule from the O_3 subunit requiring only 0.249 eV of energy. In fact, MD simulations performed on AuO_5^- at thermal energy show very fast fragmentation of O_2 indicating metastable character of the AuO_5^- .

Referring to the mass spectrum in Figure 2, the only species with one gold atom present are AuO^- , AuO_2^- , and AuO_3^- . Their relative intensities correlate well with the calculated binding energies per atom which are presented in Table 1. The peaks corresponding to AuO_2^- and AuO_3^- have almost equal intensities and very similar calculated stabilities, as reflected in the values of binding energies per atom of 2.06 and 2.19 eV, respectively. The AuO^- peak is considerably less intense in

**Figure 4.** Dissociation energies of AuO_n^- for fragmentation of (a) atomic and (b) molecular oxygen.

agreement with lower stability of only 0.97 eV. The remarkable feature in the mass spectrum is the total absence of the peaks corresponding to AuO_4^- and AuO_5^- , although theoretical calculations provide non-negligible stabilities. A reason for this might be of kinetic nature, namely, after formation, the clusters may have a significant excess of internal energy which is removed in collisions with helium. However, if the cluster has a low energy fragmentation channel, the lifetime might be shorter than the time needed for cooling, and therefore, a rapid decay takes place. The energies for fragmentation of atomic and molecular oxygen are shown in Figure 4.

Both AuO_4^- and AuO_5^- have a low energy fragmentation channel for the loss of molecular oxygen. It should be emphasized, however, that the values shown correspond to the reaction products in their thermodynamically most stable states. The value for AuO_4^- is 0.427 eV, leading to AuO_2^- in its most stable triplet state and to molecular oxygen also in the triplet state. This reaction is however spin-forbidden, and the spin allowed dissociation channel leading to the singlet structure of AuO_2^- , in which the oxygen is adsorbed molecularly, has a significantly higher dissociation energy of 1.922 eV. This may indicate that, although thermodynamically not so unfavorable, the fragmentation of molecular oxygen from AuO_4^- might actually involve a high barrier. The energy needed for fragmentation of molecular oxygen from AuO_5^- is only 0.249 eV, and MD simulations show that the O_2 molecule is easily lost under thermal conditions, which is a possible alternative explanation to account for the absence of the AuO_5^- peak from the mass spectra.

Reactions of Oxidized Gold Atoms with CO Molecules.

Upon establishing the binding characteristics of oxygen to the gold cluster anions, reaction kinetic investigations between oxidized gold-atom anions and CO were undertaken for species of the form AuO_n^- where $n = 1-3$. The resulting spectra from the investigations on the atomic gold anion are shown in Figure 5.

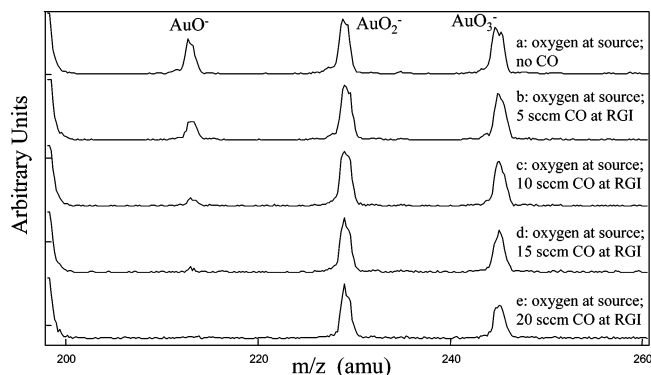


Figure 5. Reactions of AuO^- with CO added at reactant gas inlet.

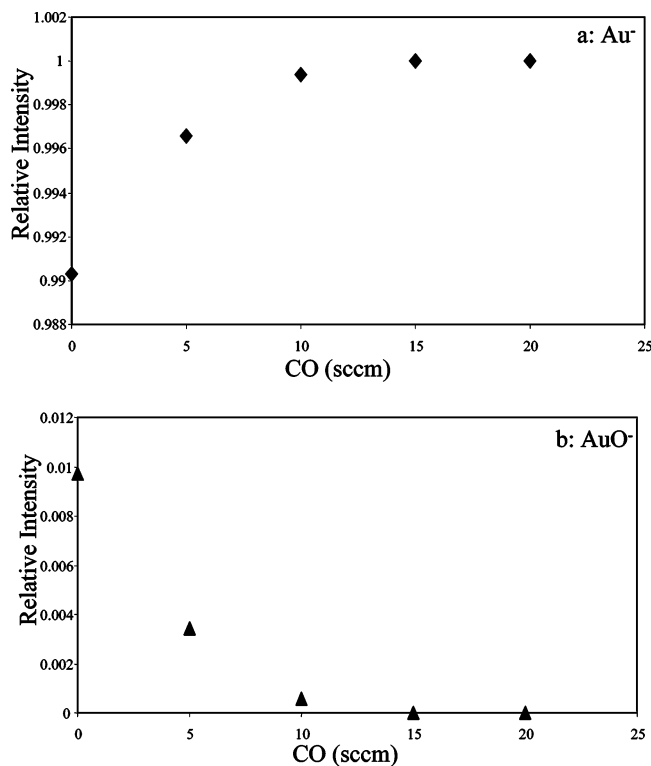


Figure 6. Branching ratio for reaction of CO with AuO^- producing Au^- .

In the top spectrum, 5a, a small amount of oxygen is seeded in the helium, and a distribution of gold oxide anions is produced. The AuO^- peak at 213 amu is found to dramatically diminish in intensity upon the addition of increasingly greater amounts of carbon monoxide. This is seen by comparing Figure 5a with b–e. As seen, addition of more carbon monoxide results in a decrease in the intensity of the AuO^- peak, but does not influence that of AuO_2^- . Furthermore, with the addition of carbon monoxide and the decrease in intensity of AuO^- and AuO_3^- , the Au^- peak increases in intensity. The branching ratios in Figure 6 show that the intensity of AuO^- decreases with CO addition. It is also shown that the Au^- intensity increases, which is a result of the reaction of CO with AuO^- and AuO_3^- . In light of the fact that the intensities of the larger bare gold clusters are low prior to reaction, the increase in Au^- is not believed to be due to the fragmentation of larger species. However, the slow decrease in the intensity of the AuO_3^- peak at 245 amu is not as evident in Figure 5. The evidence of this reaction is revealed by a very careful investigation of variations in ion intensity with CO addition.

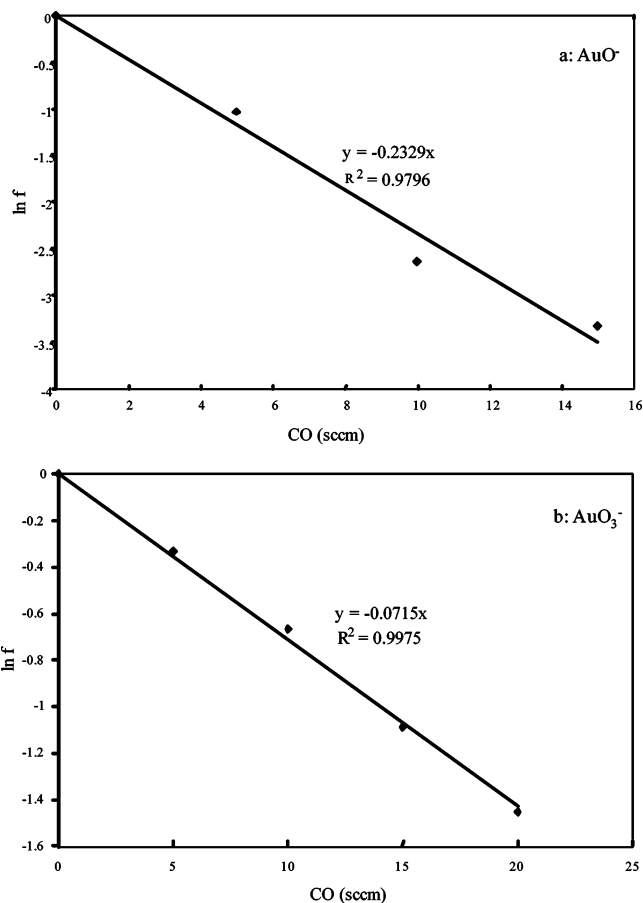


Figure 7. Kinetic plots for reactions of (a) AuO^- and (b) AuO_3^- with CO. Natural Log of relative ion intensity versus sccm CO.

The rates of reaction of carbon monoxide with AuO^- and AuO_3^- were determined assuming pseudo-first-order kinetics in view of the large excess of the CO reactant gas employed in the measurements. The reaction rate may be expressed by the following equation

$$\ln \frac{I}{I_0} = -k[\text{CO}]t \quad (1)$$

where I and I_0 are the intensities of the ion with and without the CO reactant gas added, respectively, and t is the measured time the ion spends in the flow tube. From the present experiments, we find the bimolecular reaction rate constant for AuO^- with CO to be on the order of $10^{-11} \text{ cm}^3\text{s}^{-1}$, whereas that for AuO_3^- is $10^{-12} \text{ cm}^3\text{s}^{-1}$. Rate determinations were made utilizing the slope from a number of plots analogous to those shown in Figure 7. From these, one can also observe the decrease in relative intensity of both AuO^- and AuO_3^- with an increase in CO addition. These plots were determined from experiments in which 1–2% oxygen seeded in helium was passed over the metal plasma and 0–20 sccm (standard cubic centimeters per minute) of CO, varied by 5 sccm increments, was introduced at the reactant gas inlet.

In order to elucidate the energetics and the mechanism for the reactivity of oxidized atomic gold anions toward CO, the energy profiles connecting reactants and products, including intermediate complexes and transition states, were determined utilizing DFT methods.

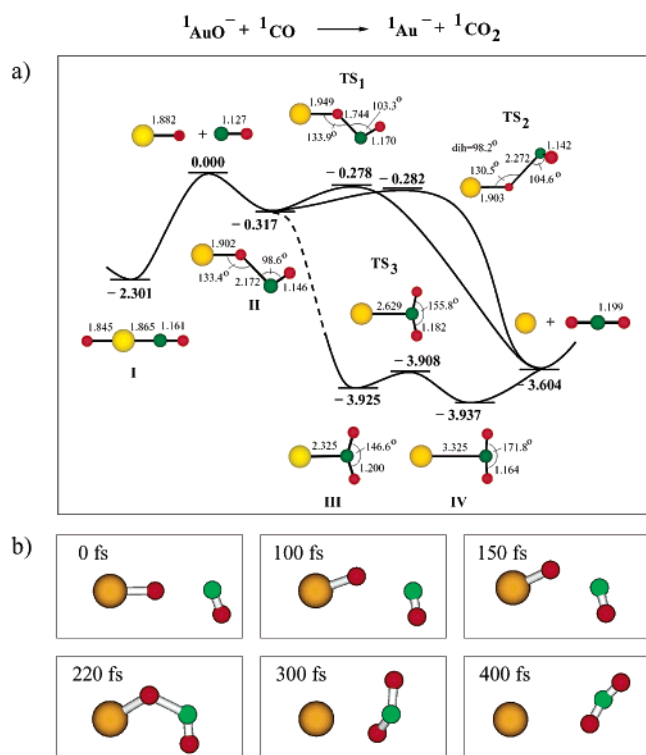


Figure 8. (a) Reaction profile and (b) MD snapshots for reactions between AuO⁻ and CO.

AuO⁻ + CO. The reaction of AuO⁻ with the CO molecule in the singlet state yields Au⁻ and CO₂ with a reaction energy of -3.604 eV (cf. Figure 8a). In the singlet state of AuO⁻, the excess electron is localized at the oxygen atom. The initial step of the reaction is a complex formation in which the CO molecule can be bound either directly to the gold atom or to the oxygen atom. It should be noted that, although the lowest energy fragmentation channel for AuO⁻ involves triplet oxygen, the dissociation energy for the singlet is considerably higher, 4.72 versus 1.94 eV. The complex where the carbon of the CO molecule is directly bound to gold has a stability of 2.30 eV (I) and does not react further due to steric effects. The other complex in which CO is bound to the oxygen atom has a stability of 0.32 eV (II) with respect to the reactants and can react following three distinct reaction pathways. Two of the reaction pathways are direct reactions in which the products (Au⁻ and CO₂) are separated from the complex by barriers with heights of 0.039 and 0.035 eV, respectively. The transition state TS₁ corresponding to the barrier of 0.039 eV has a structure related to the initial complex with an elongated Au–O bond and shortened C–O bond and is a direct precursor for formation of Au⁻ and CO₂. The second transition state TS₂ has a partially elongated C–O bond, and the CO group is rotated out of the Au–O–C plane. This leads to the breaking of the Au–O bond and formation of CO₂. Notice that the excess electron along the above reaction pathways remains on the CO₂ subunit before fragmentation into Au⁻ and CO₂ occurs. In the third reaction pathway, the carbon atom exchanges location with oxygen, forming a bond with the gold atom. The search for the barrier involved in this rearrangement has been carefully carried out and the transition state has not been identified. We assume that the barrier either does not exist or it is very low as indicated by the MD simulations in which the exchange of the Au–O bond

with the Au–C bond takes place easily. The formed complex has a stability of 3.925 eV (III), and the CO₂ unit has a bent structure indicating significant charge transfer from gold. In the next step, charge is transferred from the CO₂ unit back to the gold atom leading to structure (IV) with weakly bound linear CO₂ which can be ejected in the last step requiring only 0.33 eV of energy.

In order to follow the reaction mechanism, ab initio MD simulations have been performed starting from a bent arrangement of AuO⁻ and CO with a large O–C distance and zero initial kinetic energy. The examination of the potential energy surface for this reaction shows that a collinear approach of CO onto AuO⁻ is hindered by a barrier of 0.1 eV whereas, in the case of nonlinear arrangement, there is no barrier for the formation of the complex. The snapshots of the reaction dynamics presented in Figure 8b show that CO binds directly to the oxygen atom of AuO⁻ forming a complex which then quickly falls apart into Au⁻ and CO₂. In summary, structural calculations as well as MD simulations show that the reaction of AuO⁻ with CO is a very fast and thermodynamically favorable reaction, leading to the oxidation of CO in agreement with the experimental findings presented here.

AuO₂⁻ + CO. The lowest energy structure of AuO₂⁻ with triplet multiplicity is linear with two terminal oxygen atoms bound directly to the gold atom. The dissociation channel for an oxygen atom is 4.22 eV. Moreover, since the ground electronic state of AuO₂⁻ is a triplet state, whereas the ground electronic states of the most stable reaction products, AuO⁻ and CO₂, are singlets, the reaction leading to formation of CO₂ is a spin-forbidden process. At most, it is expected to proceed with a small reaction rate (or not react at all) which is dependent on the strength of the spin–orbit coupling between the singlet and triplet electronic states along the reaction pathway.

Two reaction pathways leading to the formation of the CO₂ in the singlet state with AuO⁻ in the triplet state are shown in Figure 9a. The reaction starts with formation of a weakly bound complex (0.14 eV) (I) which is separated by a transition state TS₁ with the barrier of 0.148 eV from the very stable complex (1.37 eV) (II) in which CO is bound to a terminal oxygen atom. After the complex formation, reaction can proceed along two different pathways. The energetically more favorable pathway involves first a step in which the O–C–O angle is first inverted, which requires surmounting the barrier of 0.197 eV corresponding to the structure with almost linear O–C–O unit (TS₃), followed by breaking of the Au–O bond which is connected with the barrier of 0.352 eV (TS₄). Along this pathway, the excess charge remains on the CO₂ subunit. The second reaction pathway involves, in the first step, breaking of the Au–O bond and simultaneous formation of the Au–C bond. The corresponding transition state is 0.284 eV (TS₂) higher in energy than the initial complex and leads to the structure in which a CO₂ unit is bound with the carbon atom to the gold atom. Similar to the case of AuOCO⁻, the CO₂ structure is slightly bent reflecting charge transfer from gold. In the next step the Au–C bond is broken leading to electron transfer from the CO₂ unit to Au⁻ and subsequent formation of CO₂. Due to the inability of the DFT methods to accurately describe weak dispersion interactions, the barrier involved in the electron transfer process is not expected to be negligible, but the weakly bound van der Waals complex between AuO⁻ and CO₂ has not

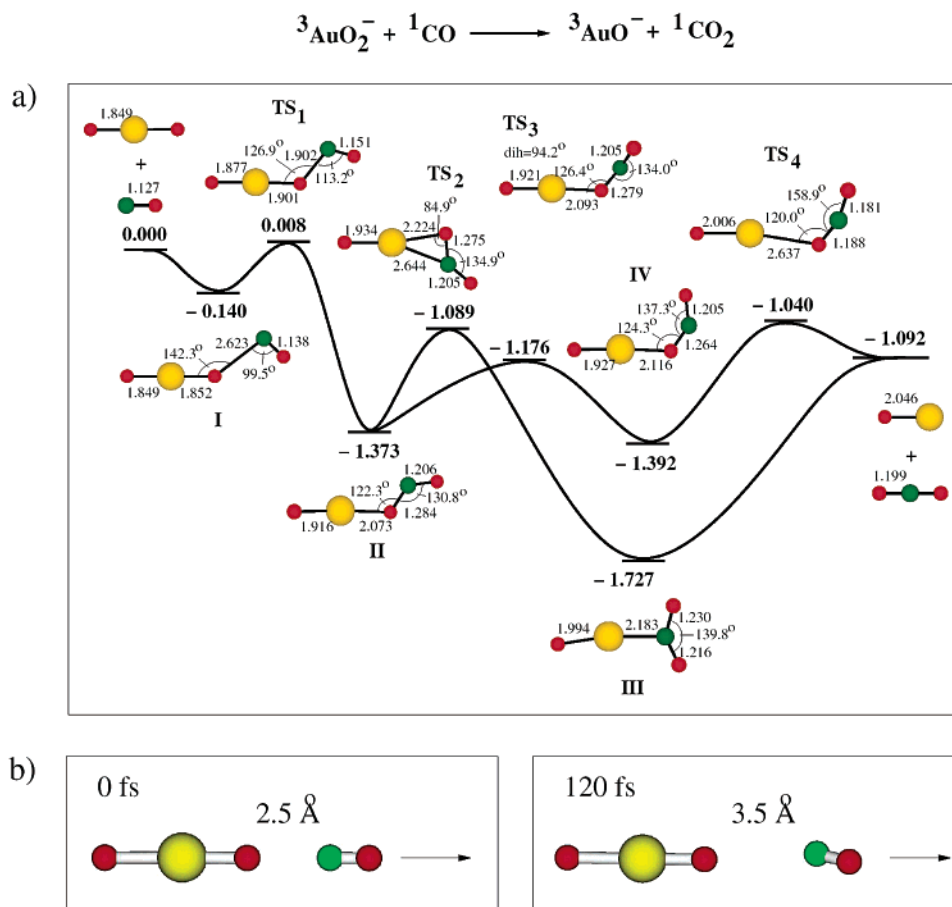


Figure 9. (a) Reaction profile and (b) MD snapshots for reactions between AuO_2^- and CO.

been identified. In contrast to the reaction of AuO^- with CO, which is highly exothermic, the reaction of AuO_2^- is exothermic only by 1.092 eV, which is a consequence of the stronger Au–O bonding in AuO_2^- . In addition, the formation of the AuO_2^- –CO complex involves a barrier (0.148 eV) which is of comparable size to the stability of the initial weakly bound complex (0.140 eV) and which, therefore, represents a critical bottleneck for the reaction. Due to this fact, and to above-mentioned spin forbidden process, it is expected that the reaction, if it takes place, would only proceed very slowly. This is confirmed by MD simulations in which neither the complex formation nor the reaction can be seen at initial conditions corresponding to well separated reactants with zero initial energy (cf. Figure 9b). Experimentally, as can be seen from Figure 5, no appreciable reactivity is observed in the case of AuO_2^- , consistent with obtained theoretical results.

$\text{AuO}_3^- + \text{CO}$. The most stable structure of AuO_3^- with triplet multiplicity can be viewed as AuO^- with molecular oxygen bound to the gold atom. The reaction with CO on the triplet surface is exothermic with a reaction energy of 2.054 eV, as shown in Figure 10a. In the first step, the reaction mechanism involves the formation of complex (I) in which the CO molecule is bound to the terminal oxygen atom bound to gold. The reaction proceeds further following two pathways related to those described above for AuO_2^- . Again, the more favorable pathway involves first the inversion of the O–C–O angle (complex II) associated with the barrier of 0.142 eV (TS_4). Complex II in which CO is bound to the terminal oxygen atom subsequently releases CO_2 . The second pathway involves the

barrier of 0.234 eV (TS_2) leading to the complex with CO_2 bound to gold through the carbon atom (III). This complex easily leads to the formation of CO_2 and its subsequent loss from the reaction complex. In both cases, the product is a triplet AuO_2^- structure in which molecular oxygen is weakly bound to the gold atom. Due to the large excess of energy released during the reaction, it is expected that the AuO_2^- formed is not stable and subsequently fragments into molecular oxygen and Au^- . This is confirmed by the MD simulations shown in Figure 10b. The simulation has been started from an arrangement in which the Au–O bond and CO are collinear and not bound. With zero initial kinetic energy, first the formation of the O–C bond is seen, which takes place within 1.3 ps, followed by very fast fragmentation in which CO_2 and molecular oxygen are formed. This is consistent with the experimental findings in which we observe the diminishing of the AuO_3^- peak and subsequent increase of the Au^- peak in the mass spectrum of Figure 5.

In summary, two basic mechanisms for the oxidation of CO in the presence of Au^- have been found for AuO_n^- ($n = 1-3$). Both involve formation of a complex in the first step in which the CO molecule is bound to the oxygen atom. In the subsequent step, however, either the Au–O bond is directly broken, which is in all three cases the pathway with lower barriers, or the rearrangement takes place in which the Au–O bond is broken and a Au–C bond is formed, leading to structures with a weakly bound CO_2 unit which can be eliminated easily. Since the reaction mechanism is common to all three cases, the difference in reactivity between AuO^- (very fast) on one side and AuO_2^-

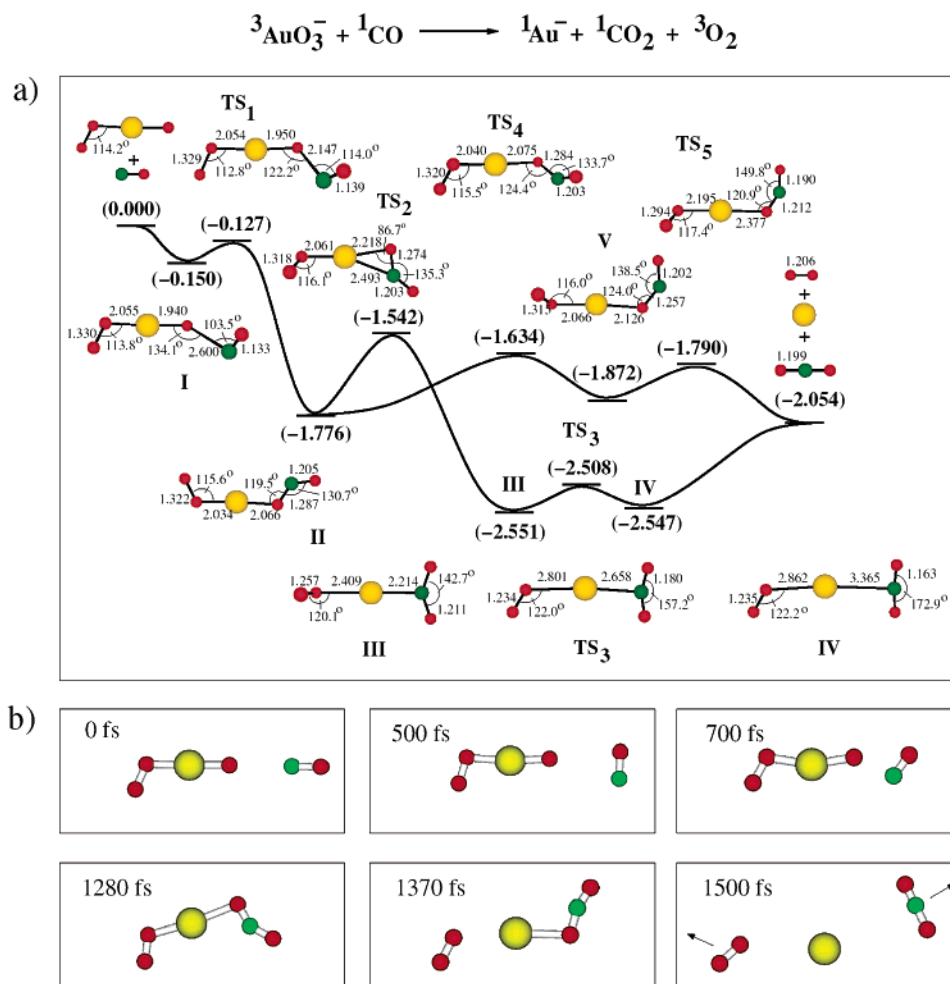


Figure 10. (a) Reaction profile and (b) MD snapshots for reactions between AuO_3^- and CO.

(very slow) and AuO_3^- (medium slow) on the other side is a consequence of quantitatively different reaction barriers.

Discussion and Conclusions

Our investigations on the uptake of oxygen onto gold cluster anions again reveal findings which differ from those presented in the literature by others.^{5,10,12,14} We observe oxygen atoms binding to all formed species. Of most interest in the present study is the finding that oxygen atoms bind to the monomer anion of gold, in contrast to what has been reported in the literature.^{5,10,14} With our experimental setup, we not only observe binding of oxygen atoms to Au^- , we also detect multiple additions. As was shown in Figure 2, the monomer anion of gold adsorbs three oxygen atoms under our experimental conditions, but not four or more.

Recall, that with our experimental setup, the oxygen is seeded in the helium and passes across the metal plasma in the source. This method of preparation could account for the different findings in the present study as the formation of oxidized clusters would not be impeded by energy barriers to reaction, and thermodynamically stable species should be able to be readily produced. Because the oxygen is introduced into the plasma at the source, some dissociation of the oxygen molecules invariably takes place. This is in keeping with the observations of Kim et al. who showed the formation of oxygen atoms under rather similar conditions.¹⁷ However, the experimental approaches of

the many other reported studies employ an inlet downstream of the cluster source for the addition of oxygen, and these groups report molecular adsorption of oxygen onto the gold cluster anions.^{5,10,14} Therefore, other factors are required to promote the dissociation of oxygen on the gold cluster anions.⁵

The results obtained by Heiz, Landman, and co-workers, on supported gold clusters,² shed some light on findings for anionic gold clusters. The proposal that the F-center defect is responsible for the charge transfer to the gold clusters could be used to explain why the use of gas-phase gold cluster anions is effective for the oxidation of carbon monoxide. Therefore, in the case of the supported clusters, which contain an extra electron, these anion vacancies promote reaction between the molecular oxygen and carbon monoxide.² The desorption of CO in the absence of oxygen has also been reported.² In contrast, because our species are preoxidized, the adsorbed carbon monoxide molecules may have a greater chance of being oxidized prior to desorption.

An interesting difference between the results from Wallace and Whetten¹¹ and those from our laboratories involves the introduction of the reactant gases. Adding the oxygen at the source, we find that gold oxide clusters are readily formed. However, addition of the oxygen at the reactant gas inlet downstream does not produce gold oxides in our experiments. Moreover, our results indicate the loss of CO_2 from the gold atom, but we do not observe peaks that correspond to AuCO_mO^- or $\text{Au}(\text{CO})_{m-1}^-$ following reaction. Instead, we observe a

decrease in intensity of the AuO^- and AuO_3^- peaks along with the enhancement of the Au^- peak. This leads to the conclusion that the reaction between the oxygen from select preoxidized gold clusters, AuO^- and AuO_3^- , and the CO added at the reactant gas inlet is taking place. The present experiments were conducted at room temperature, and we do not observe any peaks corresponding to $\text{Au}_n(\text{CO})_m(\text{O}_2)_x^-$ as Wöste et al. reported from experiments at 100 K.¹²

Because of the unique oxygen adsorption observed in our experiments, we were able to investigate the reactivity of the monomer, which has not been reported in great detail previously in the literature. The reaction of Au^- with oxygen and carbon monoxide, which we observe in the gas phase, is in agreement with a previous study by Ozin and co-workers who found that deposited neutral gold atoms are reactive with carbon monoxide and oxygen.²⁹ Furthermore, the slow disappearance of the AuO_3^- in our study provides further evidence for the oxidation of CO in the presence of a single gold atom.

Theoretical calculations explain these experimental findings and allow us to establish a general mechanism valid for the oxidation of CO on AuO_n^- ($n = 1, 3$). This mechanism is based on the binding of CO on preoxidized Au^- , permitting easy CO_2

loss due to the facile cleavage of either a Au–O or Au–C bond. The reaction of AuO^- with CO is highly exothermic, proceeding without significant energy barriers in a direct way as shown on the reaction profiles in Figure 8a, and as also evidenced by the MD simulations. The AuO_2^- reaction proceeds with an extremely low rate due to the relatively high barrier involved in the complex formation and the forbidden crossings between the singlet and triplet potential energy surfaces. For AuO_3^- , the same mechanism applies, but the reaction is considerably slower. This is attributed to the heights of the involved barriers, but the reaction is not impeded by spin restrictions. In addition, the final product of this reaction is a bare Au^- which is formed after the relatively easy fragmentation of molecular oxygen, as observed in the experiment.

In summary, our joint experimental and theoretical findings provide evidence that select preoxidized Au^- can serve as an effective active center for the oxidation of CO having a rate which is sensitive to oxygen saturation.

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