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Interactions of CO with $Au_nO_m^-$ ($n \geq 4$)

M.L. Kimble[a], A.W. Castleman Jr.[a,*], C. Bürgel[b], V. Bonačić-Koutecký[b]

[a] *Departments of Chemistry and Physics, Pennsylvania State University, 104 Chemistry Building, University Park, PA 16802, USA*
[b] *Humboldt Universität zu Berlin, Institut für Chemie, Brook-Taylor Straße 2, D-12489 Berlin, Germany*

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Abstract

The interactions between $Au_nO_m^-$ ($n \geq 4$) and CO are presented in a joint experimental and theoretical study. Experimental investigations reveal that oxygen in both the atomized and molecular forms adsorbs onto the gold clusters but shows no sign of an uptake pattern with cluster size. Furthermore, $Au_nO_m^-$ with an odd number of oxygen atoms contain multiple CO molecules; however, in most cases, clusters with an even number of oxygen atoms are not observed to have multiple CO molecules attached. This is supported by theoretical investigations for the selected examples of $Au_4O_2^-$ and $Au_4O_3^-$.

Keywords: CO oxidation; Gold cluster; Cluster reaction; Gas phase

1. Introduction

The oxidation of CO in the presence of gold has received much attention in both the condensed and gas phases [1–27]. The aim of these studies is to understand the mechanisms and fundamental characteristics responsible for the enhanced activity and selectivity of gold catalysts, and it is expected that the insight gained will aid in developing more efficient catalysts.

Utilizing temperature programmed desorption studies of size-selected Au_x on a MgO surface, Heiz and coworkers found that the oxidation of CO is size-dependent, with Au_8 being the smallest size cluster to promote the reaction [10]. Along with Landman and coworkers, they also conducted DFT studies to reveal that a charge transfer takes place, and the cluster becomes charged via partial transfer of an electron from the oxide support. Furthermore, Heiz, Landman, and coworkers propose that these features, along with the presence of F-center defects and the dissociation of O_2 in the presence of CO, are essential in the activation of catalytic gold [10].

Wallace and Whetten have examined the oxidation of CO in the presence of gas phase gold clusters, providing evidence that Au_6^- is the smallest size species to promote the reaction [11]. They found that CO and oxygen cooperatively coadsorb, as opposed to competing for sites on the gas phase gold cluster anions. Moreover, they propose a reaction mechanism which involves dissociation of O_2 and the appearance of peaks in the mass spectrum that correspond to $Au_nO_mCO^-$. With the oxidation of CO, Wallace and Whetten observe the recovery of $Au_n(CO)_{m-1}^-$ [11].

Finally, Wöste and coworkers have performed similar studies utilizing a rf-ion trap mass spectrometer [12,13]. Through their studies of mass-selected gold cluster ions and CO, Wöste and coworkers also observed the temperature-dependent appearance of $Au_x(CO)_y(O_2)_z^-$ and the metastable intermediate, $Au_2CO_3^-$ [12,13].

Although numerous studies have been conducted in both the condensed and gas phases, the mechanisms and processes responsible for the enhanced activity and selectivity of gold for the oxidation of CO are not well understood. Utilizing model systems such as gas phase clusters, it is believed that complementary information to traditional surface science studies may be obtained in order to understand and design better catalysts [28,29]. In this context, we present preliminary results for reactions between CO and $Au_nO_m^-$ ($n \geq 4$).

2. Experimental and computational details

Utilizing a fast-flow reactor mass spectrometer, interactions between CO and gold oxide anions were carried out. The exper-

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[*] Corresponding author. Tel.: +1 814 865 7242; fax: +1 814 865 5235.
E-mail address: awc@psu.edu (A.W. Castleman Jr.).

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imental apparatus has been discussed in detail previously, and only a brief description will be given here [30–32]. Preoxidized gold cluster anions are produced in a laser vaporization source by passing oxygen seeded in helium over the metal plasma formed from the ablation of a rotating and translating gold rod. Carbon monoxide is introduced in increasing amounts (0–200 standard cm^3 min^{-1} (sccm) range over 10 sccm increments) via a reactant gas inlet which is located downstream of the cluster source. Most of the species and the buffer gas are pumped off by a high volume roots blower, but the surviving species are sampled through a 1 mm orifice and analyzed by a quadrupole mass spectrometer. The products are subsequently detected utilizing a channel electron multiplier.

The structural properties of the $Au_4O_{2,3}^-$ clusters as well as their complexes with CO have been studied using DFT methods with Becke's hybrid three parameter nonlocal exchange functional and the Lee–Yang–Parr gradient corrected correlation functional (B3LYP) (for details cf. [32,33]). Previous theoretical work has shown that this method provides the appropriate accuracy needed for determining binding energies as well as studying structure–reactivity relationships [15].

3. Results and discussion

The introduction of oxygen into the metal plasma formed from the ablation of the gold rod produced gold oxide clusters with oxygen in both the atomized and molecular forms. This was evidenced by the fact that species with a single oxygen atom are produced in the source and from earlier collision induced dissociation (CID) studies on species containing an O_2 [32–34]. CID is performed by subjecting the gold oxides produced in the laser vaporization source to a flow of inert nitrogen in the octopole of a guided ion beam mass spectrometer. The resulting fragments verify structural features, such as the existence of molecular or atomized oxygen. The resulting spectra from the addition of oxygen to Au_n^-, shown in Fig. 1, contain oxides of gold clusters Au_n^- with $n = 4$–16. As shown, multiple oxygen atoms or molecules attach to each cluster, but we do not observe a definitive trend with respect to the number of oxygen atoms or molecules with cluster size. With the addition of CO at the reactant gas inlet located downstream of cluster formation, some of the oxide species decrease in intensity or disappear from the mass spectrum, while species of the form $Au_nO_m(CO)_x^-$ appear and either increase in intensity or decrease with further CO addition. Furthermore, there are interactions taking place in which $Au_n(CO)_x^-$ species are formed, and the formation of such species possibly points toward an oxidation, association, or replacement reaction. Of these three possible reaction pathways, the oxidation and association mechanisms both have a favorable impact on catalytic reactions. However, a replacement reaction would provide evidence that the species being studied would not be a desirable catalytic surface site, as carbon monoxide would replace oxygen on the surface and block active sites. In previous work on smaller clusters, we found that oxidation is the only

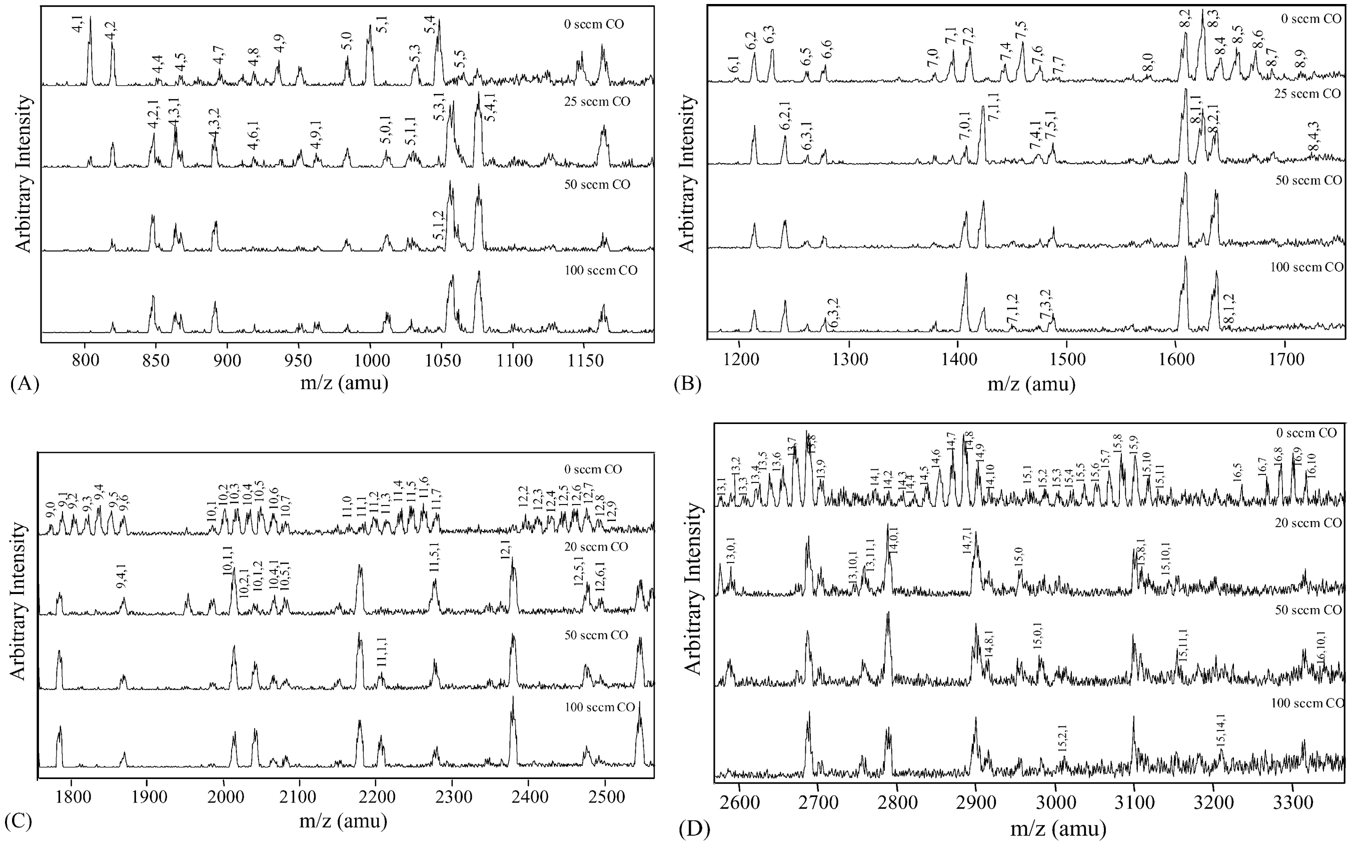

Fig. 1. Reactions for $Au_nO_m^-$ for: (A) $n = 4$ and 5; (B) $n = 6$–8; (C) $n = 9$–12; (D) $n = 13$–16. Each spectrum has oxygen introduced at the source and increasing amounts of CO added at the reactant gas inlet. Labels correspond to $Au_nO_m(CO)_x^-$.

reaction pathway for certain $Au_{1,2}O_m^-$, while association and replacement reactions may be significant for selected $Au_3O_m^-$ species [32–34]. Therefore, from the previous studies on Au_{1-3}^- and the preliminary studies on the larger species reported herein, we can conclude that there is a size dependence in the observance of association and replacement reaction channels that occurs at $n = 3$.

Upon closer inspection of the reactions for $Au_8O_m^-$ in Fig. 1B, it is seen that, compared to $Au_{4-7}O_m^-$, there are fewer species produced as a result of the addition of carbon monoxide to the gold oxide octamers. This is of interest in the context of the work by Heiz and coworkers and will be the topic of further study from our laboratories [10]. Therefore, the smaller number of species present after the addition of CO to $Au_8O_m^-$ may be the result of more efficient reactions. This trend continues for most of the larger clusters, as there are fewer species present after CO addition for most $Au_nO_m^-$, $n \geq 8$. However, Au_{10}^- does not seem to follow the same trend, and there are considerably more $Au_{10}O_m(CO)_x^-$ products formed after CO addition, as seen in Fig. 1C.

Another notable observance from these data and from studies in which an excess amount of CO is added at the reactant gas inlet is the formation of species with multiple CO molecules attached to the gold oxide. In most cases, the only species that contain more than one CO molecule are those clusters that have one or three oxygen atoms attached. From studies with the addition of excess CO, we have looked at multiple CO molecules on $Au_nO_m^-$ ($n = 4$–10) and found this to be the case for $Au_4O_3^-$, Au_5O^-, $Au_6O_3^-$, Au_7O^-, $Au_7O_3^-$, Au_8O^-, $Au_8O_3^-$, and $Au_{10}O^-$. However, for species with $n = 4$–7 and 9–10, we observe no instances in which a cluster with an even number of oxygen atoms, either in the atomized or molecular form, contains more than one CO molecule. Nevertheless, the anionic octamer of gold is the exception. Here, $Au_8O_4^-$ and $Au_8O_6^-$ are found to have multiple CO molecules attached. Furthermore, the octamer oxides are the only species that contain three CO molecules in our studies, and we will expand our analysis to examine these in future studies.

In order to support the experimental findings on multiple CO molecules on certain clusters, we have chosen the examples of $Au_4O_2^-$ and $Au_4O_3^-$ for theoretical investigation of the interaction between gold clusters and a number of CO molecules. We present stable structures and binding energies of $Au_4O_2^-$ and $Au_4O_3^-$ with one and two CO molecules in Fig. 2. The first CO molecule binds strongly to $Au_4O_2^-$ and $Au_4O_3^-$ with energies of 1.889 eV and 1.278 eV, respectively (cf. Fig. 2). In general, if a stable O–Au–C–O subunit can be formed, binding of CO onto the gold oxide clusters is highly favorable, leading to very stable carbonyl complexes (BE > 1.2 eV). This is due to the fact that the Au atom in such an O–Au-group is strongly positively charged, a condition that is desirable for binding of CO which acts in this case as a $2e^-$ donor. Notice that the energy gained by adsorption of CO leads to a pronounced rearrangement of the cluster geometry itself. This process occurs without substantial kinetic barriers, which has been demonstrated by MD simulations on the example of $Au_4O_2^-$ and CO as shown in Fig. 3. However, the binding situation is changed when CO binds to a Au–Au subunit; the peripheral Au atom, which binds the CO molecule, is partially negatively charged. Therefore, a weak charge transfer from the cluster towards the CO molecule takes place, leading to low binding energies and a bent geometry of the carbonyl complex. Since the formation energy of such carbonyl complexes is usually not high (∼0.5 eV), the cluster geometry does not change much, as can be seen for $Au_4O_2(CO)_2^-$ (Fig. 2). Due to the fact that it is not possible to have two O–Au–CO groups in $Au_4O_2(CO)_2^-$ or $Au_4O_3(CO)_2^-$ preserving the low coordination number for gold atoms, the binding energies are substantially lower (0.566 eV versus 0.824 eV). In

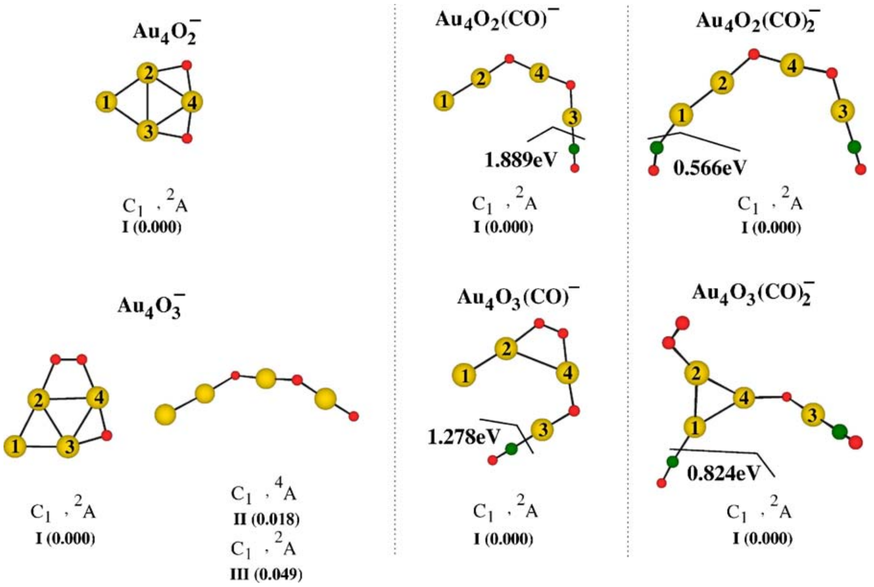

Fig. 2. Lowest energy structures of $Au_4O_{2,3}(CO)_{0-2}^-$. Shown are isomers lying within 0.2 eV. Symmetry and spin state are given as well as relative energy with respect to the most stable structure. Binding energies for CO association are shown in bold, and gold atoms are labelled for illustrating purpose to show to which Au atom CO is bound.

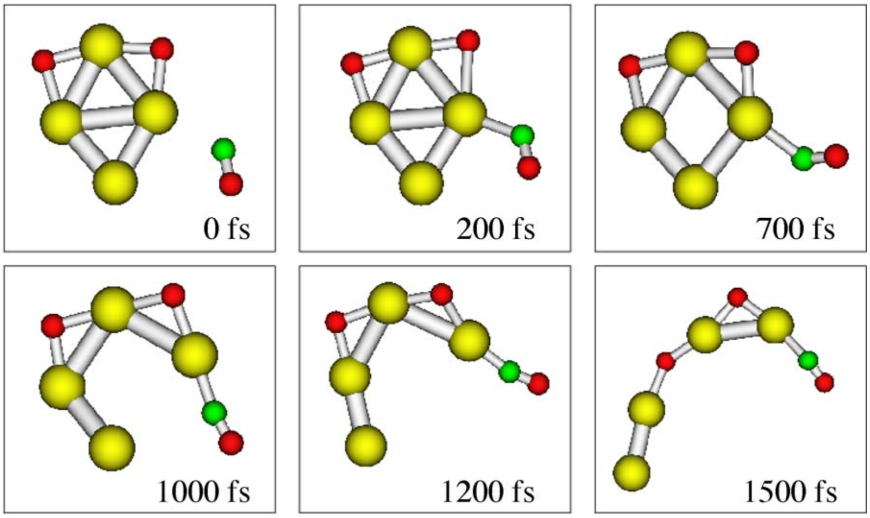

Fig. 3. MD simulation for the adsorption reaction of $Au_4O_2^-$ with CO. Notice that the cluster geometry is rearranging from a rhombic (0 fs) to a [3 + 1] gold skeleton.

conclusion, CO molecules are strongly bound as long as there are free accessible adsorption sites leading to stable carbonyl complexes with O–Au–CO subunits, and therefore, interaction is dependent on the geometric and electronic structure of the complex.

The above presented theoretical results support the experimental findings in that only one CO molecule binds to $Au_4O_2^-$, since the binding energy of the second CO molecule is considerably lower and lies under the value for which association in our experiment may be observable. In the case of $Au_4O_3^-$, in addition to the first CO, the second binds over this limit and therefore has been observed.

The presented results are only a beginning effort in unraveling the fundamental characteristics responsible for the observed interactions between CO and $Au_nO_m^-$ ($n \geq 4$). Further experimental and theoretical work must be completed in order to definitively recognize reaction pathways.

4. Conclusions

The reactions between preoxidized gold cluster anions, $Au_nO_m^-$, with $n \geq 4$ have been investigated utilizing a fast-flow reactor mass spectrometer, and theoretical studies have been carried out to support the experimental findings. The results of the experimental studies reveal that multiple oxygen atoms adsorb onto the gold cluster anions. These clusters contain oxygen in both the molecular and atomized forms due to its addition into the laser vaporization source. The results do not, however, show any pattern of oxygen addition with cluster size.

Upon the addition of CO at the reactant gas inlet, products that are the result of either CO oxidation, association, or replacement of oxygen by CO are observed. This is in accord with recently reported results from our groups in which we revealed that selected monomer and dimer oxides react with CO to produce CO_2 [32–34] while the trimer oxides interact with CO through association or replacement reactions [33,34]. Another interesting finding involves the reactive behavior of cluster anions which evidently changes at Au_8^-. These results may be found to have significance regarding the role of size on the reactivity of gold for the oxidation of CO and will be the topic of further study.

Through these investigations and studies in which an excess amount of CO is added, we observed the appearance of peaks that correspond to the uptake of multiple CO molecules on select $Au_nO_{1,3}^-$ species. However, this usually only occurs for species with $n = 1$ and 3 (the exceptions being $Au_8O_{4,6}^-$). Theoretical investigations for the examples of $Au_4O_2^-$ and $Au_4O_3^-$ allowed us to establish a connection between the geometric and electronic properties of the gold oxide cluster and its ability to bind CO, supporting the experimental findings. With the presented mechanism, we revealed that $Au_4O_2^-$ will only adsorb one CO, while $Au_4O_3^-$ will bind two CO molecules.

The studies reported herein are the start of a more extensive investigation of the reactivity of anionic gold oxide clusters with CO. With the addition of the selected ion flow tube or the use of a guided ion beam mass spectrometer [35], mass selection experiments as well as detailed kinetic analysis will be performed in order to identify the reaction pathways for individual species. This information will aid in gaining a further understanding of reaction mechanisms in order to provide insight into the tailoring of efficient and selective gold catalysts.

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