

# Chemisorption of atomic and molecular oxygen on Au and Ag cluster anions: discrimination of different isomers

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## Abstract

Structures of coinage metal clusters reacted with atomic and molecular oxygen were studied using Ultraviolet Photoelectron Spectroscopy and Density Functional Theory calculations. We show that O<sub>2</sub> partially dissociates on Ag<sub>2</sub><sup>-</sup>, and this dissociative chemisorption is a kinetically hindered step. For Au<sub>4</sub>O<sub>2</sub><sup>-</sup>, in addition to the previously observed molecularly adsorbed oxygen, we are now able to synthesize a second isomer using atomic oxygen reagents, in which oxygen adsorbs dissociatively. We demonstrate that different isomers can be distinguished by comparative studies of chemisorption of atomic and molecular species on metal clusters, which is otherwise difficult.

Chemical properties of nanoclusters of noble metals have attracted particular attention due to their interesting cluster size effects [1–11]. Au, the most inert material in bulk form, becomes extraordinarily active for various catalytic reactions when its particle size is confined to few nanometers [1–3]. Ag exhibits analogous cluster size effects for catalytic activities [12]. Even though extensive studies have been performed on nanocatalysis of coinage metals such as Au and Ag, the mechanisms of various reactions on Au and Ag nanoparticles have not been unveiled. This is due to the fact that spectroscopic evidence for important elementary steps in catalysis such as O<sub>2</sub> chemisorption on Au and Ag nanoparticles was missing. It has been suggested that efficient dissociation of O<sub>2</sub> on Au-nanoparticles is the key of Au-nanocatalysis [1,6]. However, non-dissociative chemisorption was also suggested in some previous studies [2,3].

Recently, Au cluster anions in the gas phase have been used as model systems to shed light on reaction mechanisms of nanocatalysis [8–11]. Gas phase clusters can be easily mass-selected and, therefore, size dependent variations of catalytic properties can be investigated on atomic scale. For Au cluster anions, it was found that only even-numbered clusters (smaller than Au<sub>21</sub><sup>-</sup>) having a lone-pair electron and a hole in the valence electronic shell react with O<sub>2</sub>, whereas the odd-numbered ones with closed shell configurations are inert [8,9,13]. This result can be rationalized by assuming that O<sub>2</sub> acts as a one-electron acceptor (superoxo-species), implying that O<sub>2</sub> molecularly chemisorbs on even-numbered Au cluster anions [8,9]. This suggestion was confirmed in our recent experimental studies, in which vibrational fine structures of O–O stretching frequencies were resolved in the photoelectron spectra of Au<sub>2</sub>O<sub>2</sub><sup>-</sup> and Au<sub>4</sub>O<sub>2</sub><sup>-</sup> [10,11]. Activated di-oxygen species were suggested to be an important reaction intermediate for catalytic reactions on Au nanoclusters. This result is quite in contrast to that on bulk Pt-group metal surfaces, on

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which dissociative chemisorption of  $O_2$  is required for the catalytic CO-oxidation [10,11].

There are still many open questions regarding chemisorption behaviours of oxygen on noble metal clusters. It has been a generally accepted view that dissociative chemisorption of oxygen is thermodynamically more favourable compared to molecular chemisorption, yet, the dissociative chemisorption can be kinetically hindered, which can be the driving force for the molecular chemisorption of  $O_2$  [6,9–14]. However, one cannot exclude the possibility that dissociative adsorption is thermodynamically less favourable than molecular chemisorption, leading to the molecular chemisorption. Recently theoretical studies were carried out to shed light on this issue, which predicted that dissociative chemisorptions of  $O_2$  on  $Au_n^-$  with  $n = 4-8$  are thermodynamically favoured than molecular chemisorption [15]. According to this theoretical study, dissociative chemisorption of  $O_2$  on  $Au_n^-$  with  $n = 4,6,8$  cannot be experimentally detected due to high activation barriers for dissociative chemisorption of  $O_2$ . On  $Au_2^-$ , in contrast, molecular chemisorption of  $O_2$  was suggested to be thermodynamically more stable than dissociative chemisorption.

In the present work, attempts were made to synthesize some isomers of  $M_nO_2^-$  ( $M = Au$  and  $Ag$ ,  $n =$  number of metal atoms), which should be formed in terms of thermodynamics, yet not detected in our previous studies as a result of kinetic hindrance. The Pulsed Arc Cluster Ion Source (PACIS) is used to produce  $M_nO_2^-$  [16,17].  $O_2$  is inserted into the electric arc, in which  $O_2$  dissociates before reacting with metal atoms evaporated from the target electrode. Metal and oxygen atoms can slowly pass through the extender, in which they can be cooled down by collisions with He carrier gas and form clusters. Using this method (which is going to be referred to as ‘atomic oxygen’ method),  $M_nO_m^-$  with  $m =$  even as well as odd numbers are detected, indicating that oxygen actually exists atomically in the gas phase. Previously, we have studied  $Au_nO_2^-$  clusters produced by inserting  $O_2$  into the chamber after Au atoms formed clusters and cooled down to about room temperature in the extender (which is to be referred to as ‘molecular oxygen’ method). In this case, only  $Au_nO_2^-$  was detected, indicating that  $O_2$  dissociation was not allowed in the gas phase [10,11]. The mass of clusters was selected using a Time-of-Flight (TOF) mass spectrometer, and the Ultraviolet Photoelectron Spectroscopy (UPS) experiments for the mass-selected clusters were performed using UV Laser pulse (Photon energy = 4.66 or 6.4 eV) [16]. The temperature of the clusters at the stage of UPS measurements is estimated to be about room temperature [16]. The resolution of our mass spectrometer is not high enough to ensure that the clusters studied in the present work are free from the hydrogen contamination. However, it should be mentioned that

attachment of hydrogen completely changes electronic structures of Au cluster anions, and, therefore, the chemisorption pattern of Au cluster anions should be sensitive to the hydrogen contamination. As long as we reproduce the previously observed even/odd-alternation in the  $O_2$  chemisorption (i.e., only even-numbered Au cluster anions react with  $O_2$ ), one can ensure that the influence of the H contamination is negligible [18].

$Ag_2O_2^-$  clusters were prepared by the aforementioned two different ways, which yielded UPS spectra in Fig. 1a,b, respectively. The vibrational fine structure between 2.2 and 4.2 eV of Fig. 1a produced by ‘molecular oxygen’ has a spacing of 170 meV, corresponding to the O–O stretching frequency, implying that the UPS spectrum in Fig. 1a involves molecular chemisorption of oxygen. The first four peaks between 2.2 and 3.2 eV are assigned to the vibrational fine structure of the neutral ground state, since these features come from transition from the anion ground state to the neutral ground state. The peaks above 3.2 eV are assigned to transitions to the first electronically excited state of the neutral cluster, and, therefore, the fine structure in this energy range is assigned to the vibration of the first excited state of the neutral. Using ‘atomic oxygen’, the peak at 3.5 eV (see arrow in the figure) increases with respect to other features at lower and higher binding energies (Fig. 1b). The difference spectrum between Fig. 1a,b created after a proper normalization procedure is illustrated in Fig. 1c. The UPS spectrum in Fig. 1c should be related to an isomer, which increases in concentration, when  $O_2$  is dissociated in the electric arc before reacting with metal atoms, i.e., the formation of this isomer is kinetically hindered. Considering that dissociative chemisorption of  $O_2$  often involves high activation barriers, we assign the spectrum in Fig. 1c to the dissociative chemisorption of oxygen. The higher Vertical Detachment Energy

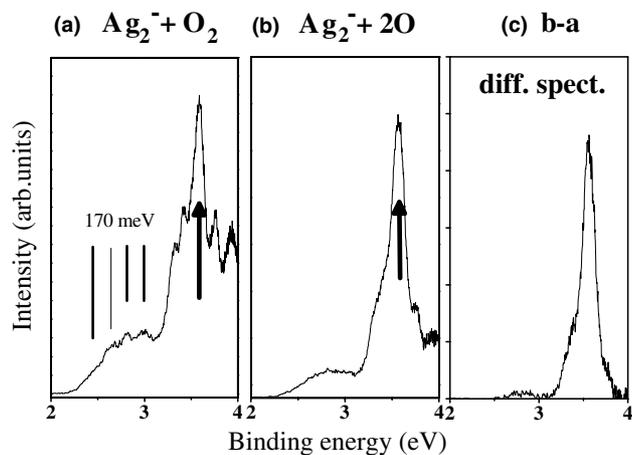


Fig. 1. UPS spectra of  $Ag_2O_2^-$  produced using molecular (a) and atomic (b) oxygen methods. (Photon energy = 4.66 eV) (c) difference spectrum (b) – (a) after a proper normalization procedure.

(VDE) of Fig. 1c compared to that in Fig. 1a is also an indication of dissociative chemisorption of oxygen, since dissociative chemisorption usually accompanies a larger metal to oxygen charge transfer than molecular adsorption [11]. This result demonstrates that one cannot completely exclude dissociative chemisorption of oxygen based on an observation of O–O vibrational progressions in UPS spectra, since UPS spectra can consist of combinations of different isomers. By changing experimental parameters, one can vary relative abundance of various isomers, which allows identifications of different isomers using UPS.

In Fig. 2a, a UPS spectrum of  $\text{Au}_2\text{O}_2^-$  produced using atomic oxygen method is displayed (Photon energy = 6.4 eV). The UPS spectrum in Fig. 2a is identical to that of  $\text{Au}_2\text{O}_2^-$  in our previous experiments, in which molecular oxygen reagents were used to create  $\text{Au}_2\text{O}_2^-$  [11]. Using a photon energy of 4.66 eV (Fig. 2b), a very strong vibrational progression with a spacing of about 180 meV dominates the binding energy range between 3 and 4.5 eV of the UPS spectrum, which we attributed to the O–O stretching frequency of a superoxo-species, indicative of non-dissociative chemisorption of oxygen [10,11]. There are two main features in Fig. 2b, one in the binding energies between 3.0 and 3.6 and the second one between 3.8 and 4.2 eV. Both features contain vibrational fine structures of about 180 meV. The 3.0–3.6 eV features can be assigned to the transitions from the ground state of the anionic clusters to the ground and the first excited state of the neutral ones. The ground and the first excited state of the neutral differ by their spin multiplicities. According to our theoretical calculations, the ground state of the anion is in a doublet state, and the transition energies to the neutral singlet and triplet states amount to 3.08 and 3.35 eV, respectively, in agreement with the binding energies of the first feature in Fig. 2b [19]. The second feature in 3.8–4.2 eV is suggested to be transitions to the non-ground singlet or triplet states of the neutral clusters, which cannot be

theoretically calculated in the present work. Note that one ends up with the ultimate ground state of each spin state in our calculations [18]. The O–O stretching frequencies of the first and the second feature are almost identical within the experimental error bar. In principle, one expects that the O–O vibrational frequencies of the first and the second feature should be different. However, our experimental resolution does not allow discriminating this difference in vibrational frequencies of the ground and the first electronically excited state of the neutral  $\text{Au}_2\text{O}_2$  clusters. Note that the error bar for the determination of the vibrational frequencies using our UPS spectra is as large as 10 meV [10].

Our observation of the O–O vibrational structure in UPS indicates that  $\text{O}_2$  molecularly adsorbs on  $\text{Au}_2^-$ , even if atomic oxygen is used, i.e., dissociation of oxygen is thermodynamically much less stable than the molecular chemisorption of oxygen. Another possible scenario is that  $\text{Au}_2^-$  selectively reacts with small amounts of  $\text{O}_2$ , which is not dissociated in the electric arc. In this case, also, our conclusion that molecular chemisorption of oxygen is thermodynamically preferred is valid. According to recent theoretical calculations, the adsorption energy of  $\text{O}_2$  on  $\text{Au}_2^-$  is determined to be 1.39 eV for the non-dissociative chemisorption, whereas that of the dissociative chemisorption amounts to 0.79 eV [15]. Even though there have been inconsistent results from experiments and various theoretical approaches about the absolute binding energy of  $\text{O}_2$  on  $\text{Au}_2^-$  [4,20,22], the general trend of the theoretical calculations that the molecular chemisorption is much more stable than the dissociative chemisorption for  $\text{Au}_2\text{O}_2^-$  is in agreement with our experimental data.

UPS spectrum of  $\text{Au}_4\text{O}_2^-$  produced by atomic oxygen is compared with that synthesized by molecular oxygen (Fig. 3b). In Fig. 3b, the peak C is nearly identical in binding energy compared to our previous results using molecular oxygen, which is displayed in Fig. 3a [11]. However, the peak B was not found in our previous experiments (Fig. 3a), and the intensity ratio of the peak A and peak C in Fig. 3b is different from that in Fig. 3a [11]. Moreover, the shapes of the peak A in Fig. 3a,b are different. In our repeated experiments, the relative peak intensity of B with respect to the peak C became sometimes smaller than that in Fig. 3b (Fig. 3c), indicating that the concentration of a less abundant isomer responsible for the peak B in Fig. 3b changes upon variations of conditions of our cluster source. Using a photon energy of 4.66 eV, non-dissociative chemisorption of  $\text{O}_2$  was identified by the vibrational progression corresponding to the O–O stretching frequency [10,11]. This result indicates that the peak C in Fig. 3b,c should come from an isomer with molecularly chemisorbed oxygen, i.e., even if  $\text{Au}_4^-$  is reacted in the atomic oxygen atmosphere, two oxygen atoms can recombine to form dioxygen species. The UPS spectrum of the new isomer

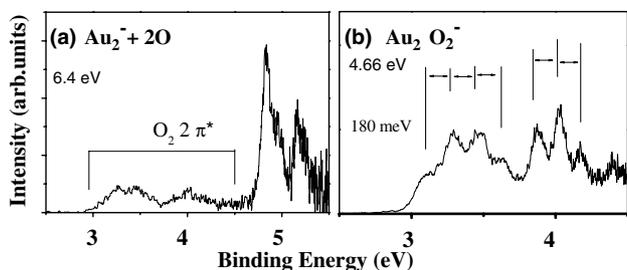


Fig. 2. (a) UPS spectra of  $\text{Au}_2\text{O}_2^-$  (Photon energy = 6.4 eV). The  $\text{Au}_2\text{O}_2^-$  was created by reaction between  $\text{Au}_2^-$  and atomic oxygen. This spectrum is identical to that of  $\text{Au}_2\text{O}_2^-$  created by reaction between  $\text{Au}_2^-$  and  $\text{O}_2$ . The features between 3 and 4.5 eV come from the  $\text{O}_2$   $2\pi^*$  orbitals, since a strong O–O vibration progression was observed in this energy regime using a photon energy of 4.66 eV (see (b), from [10]). The peaks at higher binding energies originate from Au. Please see [10,11].

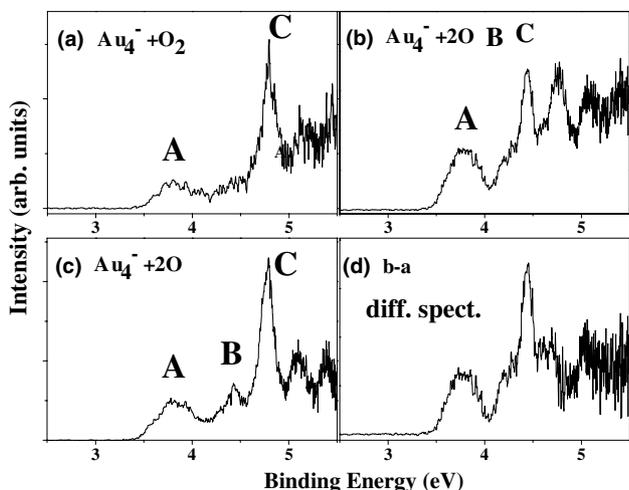


Fig. 3. (a) UPS spectra of  $\text{Au}_4\text{O}_2^-$  (Photon energy = 6.4 eV) created using molecular oxygen. (b), (c)  $\text{Au}_4\text{O}_2^-$  species were created using atomic oxygen. In our repeated experiments, two different UPS spectra displayed in (b) and (c) can be observed. (d) The difference spectrum between (b) and (a) ((b) – (a)).

responsible for appearance of the peak B in Fig. 3b,c can be extracted by producing a difference spectrum between Fig. 3b,a after a proper normalization procedure (Fig. 3d). Assuming an identical cross section of the photoemission process for both  $\text{Au}_4\text{O}_2^-$  isomers, it can be suggested that the relative concentration of the new isomer responsible for the peak B in Fig. 3b can be roughly as high as that of the isomer in Fig. 3a. It is important to note that according to the theoretical calculations, the adiabatic Electron Affinity (EA) of  $\text{Au}_4\text{O}_2^-$  with the dissociatively chemisorbed oxygen is 3.45 eV, which agrees with the experimentally determined value from Fig. 3c within 0.1 eV (Figs. 3 and 4) [15]. Therefore, we can assign the UPS spectrum in Fig. 3d to the dissociative chemisorption of oxygen on  $\text{Au}_4^-$ . At a first glance, it

is surprising that the dissociative (Fig. 3d) and molecular chemisorption (Fig. 3a) of oxygen on  $\text{Au}_4^-$  yield almost identical EAs. It is possible that the Au-tetramer framework reconstructs upon addition of two oxygen atoms, causing a decrease of EA, and this compensates the increase of EA as a result of the dissociative chemisorption of oxygen. One can also argue that a less abundant isomer of bare  $\text{Au}_4^-$  becomes thermodynamically more stable than the originally most stable  $\text{Au}_4^-$  isomer when two oxygen atoms are attached to the  $\text{Au}_4^-$  clusters. A large change of the  $\text{Au}_4^-$  framework upon dissociative chemisorption of oxygen with respect to that of the bare  $\text{Au}_4^-$  cluster is also found from theoretical calculations (Fig. 4) [15].

According to the theoretical calculations [15], the dissociative chemisorption of  $\text{O}_2$  on  $\text{Au}_4^-$  is thermodynamically more stable than the molecular chemisorption by 0.78 eV (chemisorption energy: 1.79 eV for the dissociative chemisorption and 1.01 eV for the molecular chemisorption), and therefore, one would expect that formation of the isomer A in Fig. 4 should be dominant with respect to the isomer B, when atomic oxygen is used. However, our experimental results show that the atomic oxygen reagents yield the isomer B as well as the isomer A, and therefore thermodynamic stabilities of these two isomers can lie closely, which contradicts the theoretical results in [15]. It is worth mentioning that theoretically calculated thermodynamic stabilities of different isomers of clusters often fail to explain experimentally observed clusters [20–22], even though calculations on electronic structures (EA, VDE) for clusters seem to be in good agreements with experiments [10,11,15,22].

To shed light on the relative stability of two isomers, we have studied theoretically the interaction of  $\text{O}_2$  with  $\text{Au}_4^-$  anion. Our procedure differs from that in [15] both in the choice of basis sets and exchange-correlation functional. We have used the self-consistent linear com-

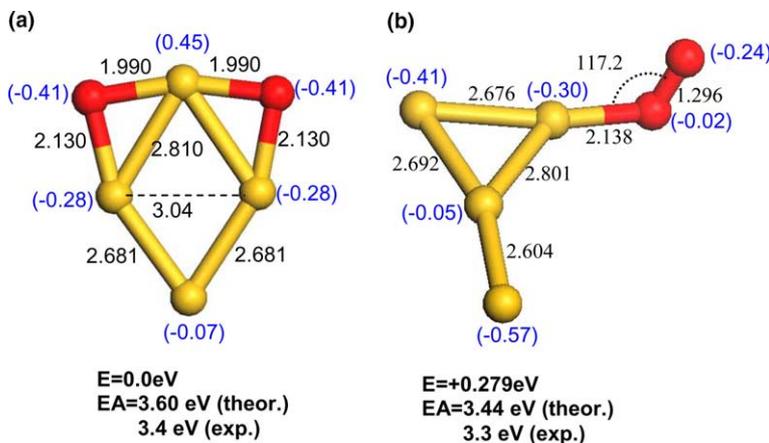


Fig. 4. The geometry parameters and charge distributions for the two degenerate isomers of  $\text{Au}_4\text{O}_2^-$  in dissociative (a) and molecular (b) states. The numbers with and without parenthesis are for charge and bond length, respectively. The relative energy ( $E$ ) and electron affinity (EA) are also given.

bination of atomic orbital-molecular orbital (SCF-LCAO-MO) approach. The total energies are calculated using density functional theory (DFT) with the generalized gradient approximation (GGA) for exchange-correlation potential, as given by Perdew–Wang 91 (commonly referred to as PW91). The atomic orbitals are represented by a Gaussian basis. We have used the 6-311++G (3df, 3pd) basis set for oxygen and the Stuttgart relativistic effective core potential basis set for gold. The exchange-correlation potential and basis set we used have been extensively tested [19]. The structures for the anion and neutral clusters were optimized without symmetry constraint using the GAUSSIAN 98 code [23]. First, we calculated the geometries of  $\text{Au}_4\text{O}_2^-$  isomers starting from the pure  $\text{Au}_4^-$  structure. This yielded the molecular adsorption state, as shown in Fig. 4b. Then, we considered another isomer which yielded the dissociative chemisorption state as shown in Fig. 4a. The energy difference between these two isomers turned out to be only 0.28 eV, which is much less than 0.78 eV reported in [15]. Note that the authors of [15] used pseudopotentials for both Au and O atoms, whereas we used all-electron basis for O atoms. A recent study claimed that hybrid functional B3LYP is better than GGA calculation with PW91 functional for Au–O system [24]. To check the effect of different exchange-correlation functional and basis set on the results, first we changed PW91 to B3LYP hybrid functional while keeping the basis set unchanged. We find that the energy difference for the two isomers is 0.285 eV, which is almost the same as our previous results. Then, we used the same basis set and functional as used in [24], i.e., 6-311 + G(3df) for oxygen and Los Alamos relativistic effective core potential (RECP) for Au. At B3LYP level of theory, the calculated energy difference for these two isomers becomes 0.163 eV. All these results indicate that the molecular and atomic oxygen adsorbed states of  $\text{Au}_4^-$  are energetically nearly degenerate. Note that the energy difference between two different isomers correspond to the internal vibrational energy of about room temperature or less, since the energy should be divided by vibrational degree of freedom of the clusters. This result reconciles our experimental observations of the mixture of both isomers under our experimental conditions.

To gain further insight into the relative stability of these two isomers in Fig. 4, we have listed the charge on the atoms and the various bond lengths. Note that in the molecularly adsorbed state (Fig. 4b), the O atom connected with Au gets very little charge ( $-0.02$  e), while in the dissociative state (Fig. 4a), the two O atoms get large charge ( $-0.41$  e). In addition, the bridging Au atom in Fig. 4a is positively charged ( $+0.45$  e). The strong Coulomb attraction between this Au atom and neighboring O atoms compensates for the energy cost for breaking the  $\text{O}_2$  bond. In this way, the dissociative adsorption state becomes energetically more favorable.

The calculated EAs are also in agreement with our experimental values.

In summary, molecular chemisorption of  $\text{O}_2$  identified in our previous studies on  $\text{Ag}_2^-$ ,  $\text{Au}_2^-$  and  $\text{Au}_4^-$  shows different UPS spectra compared to chemisorption of atomic oxygen on these clusters. In the case of  $\text{Ag}_2^-$ ,  $\text{O}_2$  adsorbs dissociatively as well as non-dissociatively, implying that if there is any chemical reactions taking place on  $\text{Ag}_2^-$ , several different isomers of  $\text{Ag}_2\text{O}_2^-$  should be considered as possible intermediates. For  $\text{Au}_2\text{O}_2^-$  molecular chemisorption of  $\text{O}_2$  is thermodynamically more favourable than the dissociative chemisorption, leading to the molecular chemisorption even in the presence of atomic oxygen reagents. For  $\text{Au}_4\text{O}_2^-$  we were able to prepare a new isomer with dissociatively bound oxygen using atomic oxygen reagents, which was theoretically predicted but has not been synthesized experimentally using molecular oxygen reagent. Catalytic reactions mediated by atomically bound oxygen on  $\text{Au}_4^-$  will be performed in the future.

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