

Au₁₀⁻: isomerism and structure-dependent O₂ reactivity

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Structure isomers of the Au₁₀⁻ cluster and their chemical reactivity with O₂ are studied using photoelectron spectroscopy under different experimental conditions. In addition to the global minimum triangular D_{3h} structure, at least three low-lying isomers (X', X'', and X''') are observed distinctly using argon tagging and O₂ titration. The D_{3h} structure has a very high electron affinity of 3.88 eV, whereas the low-lying isomers have lower electron affinities (2.86, 3.09, and 3.45 eV for X', X'', and X''', respectively). It is found that the D_{3h} global minimum does not react with O₂ and can only form a physisorbed Au₁₀(O₂)⁻ van der Waals complex under cold experimental conditions. The three low-lying isomers are reactive with O₂ and can be systematically titrated out of the cluster beam using an O₂-seeded carrier gas, leaving a clean D_{3h} Au₁₀⁻ beam.

I. Introduction

Atomic clusters have been considered as well-defined model systems for obtaining insight into the molecular processes taking place in real world catalysts. In order for clusters to be effective model systems, understanding their detailed electronic, structural, and chemical properties is a prerequisite. Gold is the most noble metal and does not react with O₂ under normal conditions.¹ Early studies on small Au_n⁻ (*n* < 22) anions by Cox *et al.*² found that certain even-sized gold cluster anions are reactive with O₂. In a subsequent kinetic investigation of O₂ reacting with Au_n⁻ clusters (*n* ≤ 7), Lee and Ervin³ were only able to obtain measurable reaction rates for *n* = 2, 4, and 6. Since the discovery of catalytic effects of supported gold nanoparticles,⁴ there has been a resurgence of research on small gold clusters trying to provide insight into the catalytic mechanisms of nanogold. In particular, Whetten and co-workers⁵ performed a more thorough investigation of the O₂ reaction with Au_n⁻ cluster anions in the size range from *n* = 2–22 and found that only even-sized clusters can adsorb an O₂ molecule except Au₁₆⁻ and Au₂₂⁻. Under saturation conditions, they found that all the reactive Au_n⁻ clusters are converted to Au_nO₂⁻ except Au₁₀⁻, for which only part of the parent clusters are reacted with O₂ to form Au₁₀O₂⁻. The observed reactivity correlates with the electron affinities of the gold clusters,⁶ leading Whetten and co-workers to propose that the even-sized clusters act as a single electron donor to O₂ to form an activated superoxide-like species in the Au_nO₂⁻ complexes. The formation of the superoxide-like Au_nO₂⁻ species has been confirmed by Gantefor and co-workers^{7,8} using photoelectron spectroscopy (PES) for *n* = 2, 4, 6, and 20.

One of the most interesting findings in the study of small Au_n⁻ clusters is the discovery of planar structures.^{9,10} Using

ion mobility and density functional theory (DFT) calculations, Kappes and co-workers⁹ showed that the most stable structures of gold cluster anions are planar up to *n* = 12, for which both planar and three-dimensional (3D) structures are observed to coexist and compete for the global minimum. These results are subsequently confirmed by a joint DFT–PES study between the Landman group and our group.¹¹ More interestingly, our high resolution PES data revealed presence of isomers in certain clusters, which were not detected by the ion mobility experiment. Specifically, we showed that the dominant isomer for Au₁₀⁻ is due to the global minimum D_{3h} isomer (10A in Fig. 1),¹¹ whereas weak, low binding energy features, which were also observed in an earlier PES study,⁶ were due to a low-lying isomer (10B in Fig. 1). The high electron affinity (*E*_{ca}) of the D_{3h} isomer suggests that the neutral D_{3h} Au₁₀ must be open shell, which has been explained by Hakkinen¹² recently using a 2D electron shell model proposed by Lievens and co-workers.¹³ The high *E*_{ca} of the D_{3h} isomer suggests that it should not react with O₂ and only the isomers with the low *E*_{ca} should react with O₂. This conjecture is consistent with the observation of Whetten and co-workers,⁵ who found that a major portion of the Au₁₀⁻ cluster beam is not reacted with O₂ even under saturation conditions.

To elucidate the isomers and the isomer-dependent reactivity of Au₁₀⁻, we have carried out a detailed PES investigation under various experimental conditions. We found that the low binding energy isomers are reactive with O₂ and can be titrated

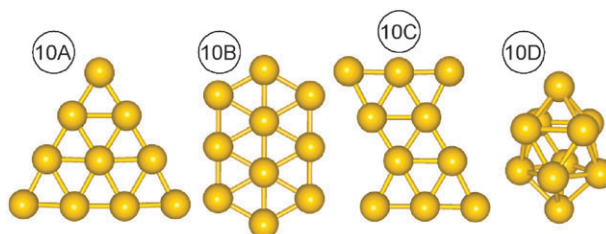


Fig. 1 Calculated structures for Au₁₀⁻. Reprinted in part with permission from ref. 11. Copyright 2003 American Chemical Society.

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out of the cluster beam to give a pure D_{3h} Au_{10}^- beam. Thus, we are able to obtain clean PES spectra for the D_{3h} Au_{10}^- cluster. Our new PES data indicate that at least three low-lying isomers co-exist in the Au_{10}^- beam and they are all reactive with O_2 . The D_{3h} Au_{10}^- global minimum does not react with O_2 and can only form a van der Waals complex with O_2 , which gives rise to PES spectra identical to the parent Au_{10}^- expected for physisorption.

II. Experimental methods

The experiment was carried out using our magnetic-bottle PES apparatus equipped with a laser vaporization cluster source.¹⁴ A gold disk target was vaporized by a pulsed laser to generate a plasma inside a cluster nozzle with a large waiting room. A high-pressure helium carrier-gas pulse was delivered to the nozzle simultaneously, cooling the plasma and initiating nucleation. Clusters formed inside the nozzle were entrained in the helium carrier gas and underwent a supersonic expansion for further cooling. After a skimmer, anions from the collimated cluster beam were extracted at 90° into a time-of-flight mass spectrometer. Clusters of interest were selected by a mass-gate and decelerated before being photo-detached by a laser beam. Photoelectrons were collected by a magnetic-bottle at nearly 100% efficiency into a 3.5 m long electron flight tube for kinetic energy analyses. For the current experiment, two detachment photon energies were used: 266 nm (4.661 eV) from a Nd:YAG laser and 193 nm (6.424 eV) from an ArF excimer laser. The photoelectron kinetic energies were calibrated by the known spectra of Au^- and subtracted from the photon energies to obtain the reported electron binding energy spectra. The electron kinetic energy (E_k) resolution of our apparatus is $\Delta E_k/E_k \sim 2.5\%$, *i.e.* ~ 25 meV for 1 eV electrons.

As we showed previously, the temperature of cluster anions is critical in determining the quality of PES spectra.^{15,16} Cold clusters yield much better resolved spectra by eliminating vibrational hot bands or low-lying isomers. We found that by carefully controlling the residence time of the clusters in the nozzle we can produce much colder clusters.¹⁷ Similar care was taken in the current experiment to yield better resolved spectra. In particular, we were able to demonstrate cluster cooling in the supersonic expansion by observing $Au_n^-Ar_x$ van der Waals complexes using an Ar-seeded helium carrier gas. To study the reactivity of Au_{10}^- with O_2 , we used O_2 -seeded helium carrier gas at different O_2 concentrations.

III. Results

III.1 Cluster cooling by Ar-tagging

One of the experimental means to confirm the presence of isomers is to vary the cluster temperature. We showed previously that we can tune the cluster temperatures somewhat by controlling the residence time of clusters in the nozzle.^{15–17} The longer the residence time the colder the clusters, because of thermalization of the nascent hot clusters inside the nozzle. In the current experiment, we used a helium carrier gas seeded with 5% argon and observed that several argon atoms can be tagged to the gold

cluster anions, demonstrating that very cold cluster anions can indeed be produced in our cluster source by controlling the cluster residence time combined with the subsequent supersonic expansion. Fig. 2 compares the 193 nm photoelectron spectra of Au_{10}^- with those tagged with one and two argon atoms. The Au_{10}^- spectrum (Fig. 2a) is similar to that reported previously.¹¹ Three weak features are clearly observed at low binding energies with vertical electron detachment energies (VDEs) at 2.88 eV for X' , 3.12 eV for X'' , and 3.49 eV for X''' . The spectra of $Au_{10}Ar^-$ (Fig. 2b) and $Au_{10}Ar_2^-$ are identical to that of Au_{10}^- , consistent with the weakly bound nature of these van der Waals complexes. Within our experimental accuracy, we could not measure any spectral shift induced by Ar in the $Au_{10}Ar^-$ and $Au_{10}Ar_2^-$ spectra. It should be pointed out that $Au_nXe_x^-$ physisorbed complexes have been observed previously by Kappes and co-workers,¹⁸ who used the Xe-tagging to perform electronic photodissociation spectroscopy of Au_nXe^- ($n = 7–11$) and observed little spectral shift relative to the bare anions.

The Ar-tagged clusters were expected to be colder than the bare Au_{10}^- . Indeed, we observed that the relative intensities of the weak features (X' , X'' , and X''') are reduced in the $Au_{10}Ar^-$ and $Au_{10}Ar_2^-$ spectra (Fig. 2), confirming that they come from low-lying isomers. In particular, the relative

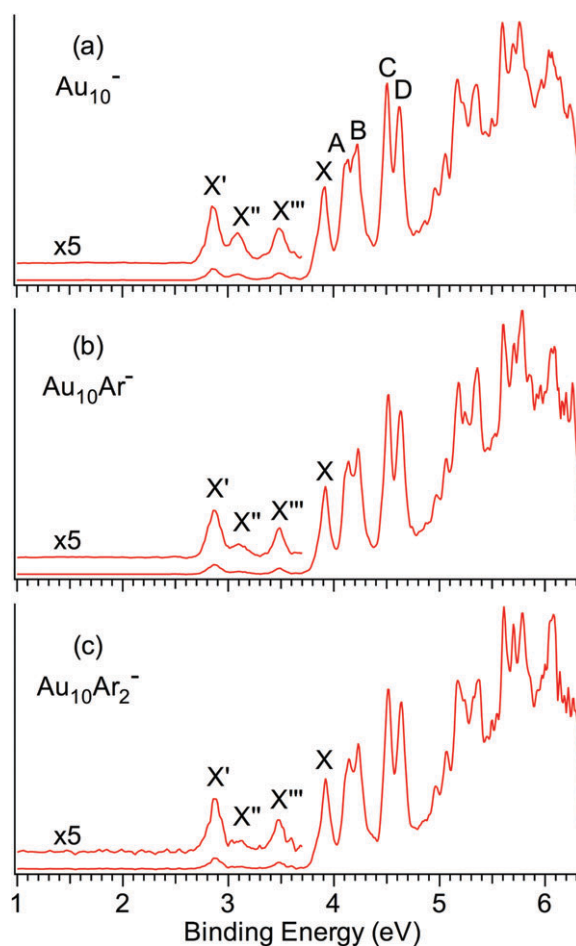


Fig. 2 Comparison of the 193 nm photoelectron spectra of Ar-physisorbed Au_{10}^- clusters (b, c) to that of the parent Au_{10}^- (a). Note the reduction of the relative intensities of the weak features (X' , X'' , X''') in the spectra of the Ar-tagged species, X'' in particular.

Table 1 Observed adiabatic (ADE) and vertical (VDE) electron detachment energies for the D_{3h} global minimum (X) and three low-lying isomers (X' , X'' , X''') of Au_{10}^- . A, B, C, D represent vertical transitions to the first four excited states of neutral D_{3h} Au_{10} . Calculated VDEs from two previous studies^{9,11} are compared with the experimental data. All energies are in eV

Obs. features	ADE ^{a,b}	VDE ^a	VDE(theo) ^c	VDE(theo) ^d
X'	2.86 (3)	2.88 (3)	2.94 (10B)	3.08 (10-II)
X''	3.09 (4)	3.12 (3)	3.14 (10C)	
X'''	3.45 (4)	3.49 (3)		
X	3.88 (1)	3.90 (1)	3.86 (10A)	4.02 (10-I)
A		4.10 (1)		
B		4.20 (1)		
C		4.50 (2)		
D		4.61 (2)		

^a The number in the parenthesis represents the uncertainty in the last digit. ^b The ADE also represents the electron affinity of the corresponding neutral clusters. ^c From ref. 11. The label in the parenthesis corresponds to the isomer label in ref. 11. ^d From ref. 9. The label in the parenthesis corresponds to the isomer label in ref. 9.

intensity of the X'' band is significantly reduced in the Ar-tagged spectra, suggesting that this isomer is higher lying. As will be shown below, X' and X''' also represent two distinct isomers. However, their intensity ratio only exhibits a slight change in the colder Ar-tagged spectra, suggesting that their energies are very close to each other, as well as close to the global minimum. The main spectral features (X, A–D, and the congested high binding energy features above 5 eV) should be all due to the global minimum D_{3h} Au_{10}^- . High binding energy transitions from the low-lying isomers (X' , X'' , and X''') should also be present, but they are negligible in comparison to the intense features of the D_{3h} isomer and are likely buried beneath the intense features in the high binding energy part of the spectra. The VDEs for the D_{3h} isomer (X, A–D) and the three low-lying isomers are given in Table 1. The adiabatic detachment energies, or the electron affinities for the corresponding neutral Au_{10} isomers are also given in Table 1.

III.2 O_2 titration of the reactive Au_{10}^- isomers

The primary purpose of this study is to elucidate the O_2 reactivity of Au_{10}^- . We used O_2 -seeded helium carrier gas to generate $Au_nO_2^-$ species. In agreement with previous observations,^{5,7,8} we also found that in the small cluster regime only even-sized Au_n^- clusters can form $Au_nO_2^-$ complexes except the Au_{16}^- cage cluster due to its high electron binding energies. We observed that the majority of each reactive Au_n^- cluster can be converted to the corresponding $Au_nO_2^-$ species except Au_{10}^- , for which the intensity of the $Au_{10}O_2^-$ complex is always weaker than the parent Au_{10}^- . Fig. 3 displays the photoelectron spectra, at two photon energies, of Au_{10}^- remained in the beam with O_2 -seeded He carrier gases, in comparison to those produced with pure He or Ar/He carrier gas (Fig. 3a and d). Using a 0.1% O_2 -He carrier gas, we observed that the weak low-binding energy features (X' , X'' , and X''') in the Au_{10}^- spectra are greatly reduced (Fig. 3b and e). With a 0.5% O_2 -He carrier gas, the weak features are almost completely gone (Fig. 3c and f). These observations indicate that the X' , X'' , and X''' features are

indeed due to low-lying isomers of Au_{10}^- , which are reactive with O_2 . These species are systematically “titrated” out of the beam with increasing O_2 concentration, leaving a clean unreactive Au_{10}^- beam. Previous studies showed that the global minimum of Au_{10}^- is the D_{3h} triangular structure (10A, Fig. 1).^{9,11} Thus, the spectra shown in Fig. 3c and f are isomer-selective, entirely due to the D_{3h} global minimum, which does not react with O_2 .

The 266 nm spectrum of Au_{10}^- (Fig. 3e) with the 0.1% O_2 -He carrier gas shows that the relative intensities of the weak low binding energy features are reduced roughly by a factor of two compared to that taken with the pure He carrier gas (Fig. 3d). However, the intensity ratios among the three low binding energy features are changed. The X'' and X''' features appear to be enhanced relative to the X' feature (Fig. 3e), suggesting that the X' isomer is more reactive toward O_2 . This observation confirms that X' and X''' represent two distinct isomers. In the Ar-tagging experiment (Fig. 2), the ratio of X' and X''' did not change significantly as a function of temperature, suggesting that these two isomers are very close in energy. But they have different reactivities with O_2 and are readily distinguished in the O_2 titration experiment.

III.3 Photoelectron spectroscopy of $Au_{10}O_2^-$: physisorption of O_2 on Au_{10}^-

Fig. 4 shows the photoelectron spectra of $Au_{10}O_2^-$ at two photon energies. Surprisingly, these spectra are identical to the isomer-selective spectra of the D_{3h} Au_{10}^- shown in Fig. 3c and f. Within our experimental accuracy, no spectral shift was observed, just like the spectra of the Ar-tagged Au_{10}^- clusters. This observation suggests that O_2 is physisorbed onto the D_{3h} Au_{10}^- cluster, unequivocally confirming its inertness toward O_2 . The low binding energy side in the $Au_{10}O_2^-$ spectra (Fig. 4) is very clean, suggesting that there is no O_2 -physisorbed Au_{10}^- derived from the X' , X'' , or X''' low-lying isomers. These isomers are reactive with O_2 , as shown in the titration experiment (Fig. 3). Hence, they likely form chemisorbed $Au_{10}O_2^-$ species, which possess high electron binding energies and should be buried beneath the Au_{10}^- spectral features. The only hint for chemisorbed $Au_{10}O_2^-$ species can be gleaned from peak A, which is slightly more intense in the spectra shown in Fig. 4 compared with the pure D_{3h} Au_{10}^- spectra (Fig. 3c and f), suggesting possible contributions from chemisorbed $Au_{10}O_2^-$ species formed by the reactive low-lying isomers. It should be pointed out that Gantefor and co-workers reported a 193 nm spectrum of $Au_{10}O_2^-$ previously⁸ and suggested charge transfer interactions between O_2 and Au_{10}^- . However, the spectrum was of low resolution and looks similar to the high resolution spectrum in Fig. 4b. Since the interpretation advanced by Gantefor and co-workers was made without realizing the low-lying isomers in the Au_{10}^- cluster, it should be reconsidered in light of the current data.

IV. Discussion

IV.1 The global minimum and low-lying isomers of Au_{10}^-

Kappes and co-workers⁹ identified two low-lying planar structures for Au_{10}^- , as shown in Fig. 1 (10A and 10B). They

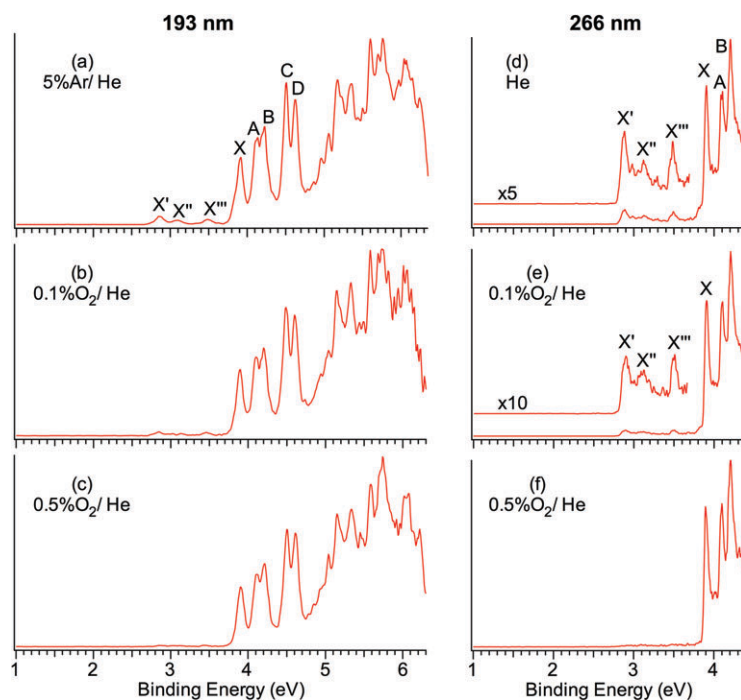


Fig. 3 Comparison of the 193 and 266 nm photoelectron spectra of Au_{10}^- produced using a 5% Ar–He (a) or pure He (d) as carrier gases with those using 0.1% O_2 –He (b, e) and 0.5% O_2 –He (c, f) as carrier gases. Note that the weak features (X', X'', and X''') are “titrated” out with increasing O_2 concentration.

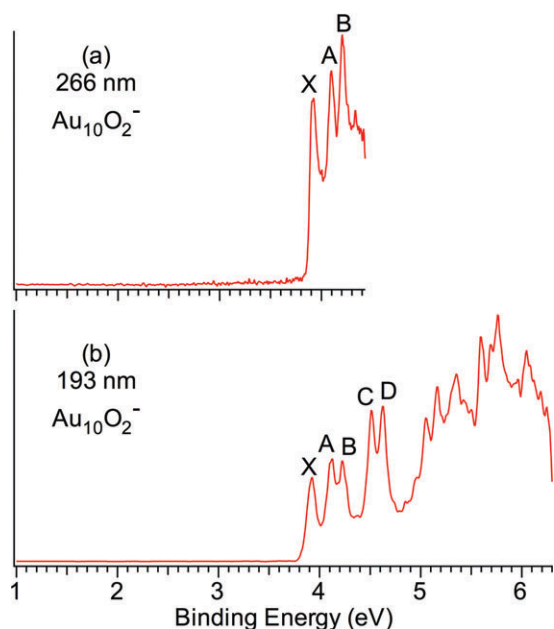


Fig. 4 Photoelectron spectra of $\text{Au}_{10}\text{O}_2^-$ at 266 nm (a) and 193 nm (b). Note the similarity of these spectra to those in Fig. 3f and c, respectively, indicating that O_2 is physisorbed in the $\text{Au}_{10}\text{O}_2^-$ complex.

referred to them as 10-I (C_{2v}) and 10-II (D_{2h}), respectively and found that the 10-I structure is the global minimum and the 10-II isomer is only 0.15 eV higher in energy. A third planar structure (10C in Fig. 1 or 10-III by Kappes *et al.*) was found to be 0.31 eV higher in energy. The lowest energy 3D isomer (10D), first considered by Hakkinen and Landman,¹⁹ was found to be 1.41 eV higher in energy. Their calculated VDE

was 4.02 eV for the global minimum 10-I and 3.08 eV for isomer 10-II. The calculated VDE for 10-I disagrees with the experimental number (2.98 eV) reported earlier by Smalley and co-workers.⁶ Based on the VDE and the ion mobility data, Kappes and co-workers concluded that isomer 10-II was the most likely candidate structure observed in their experiment. In the subsequent joint DFT–PES study on Au_n^- ($n = 4$ –14) clusters,¹¹ the same set of structures were found as shown in Fig. 1. The global minimum (10A) was found to possess D_{3h} symmetry. The low-lying planar isomers, 10B (D_{2h}) and 10C (C_{2h}), were found to be 0.12 and 0.33 eV higher, respectively, whereas the 3D isomer 10D (C_{4v}) was also found to be much higher in energy by 1.27 eV. More importantly, the low-binding energy features were correctly recognized as due to low-lying isomers while only the intense features starting from the X band and higher were assigned to be from the main isomer. The calculated VDE of 3.86 eV for the global minimum 10A was in excellent agreement with the VDE of the X band at 3.90 eV (Table 1). The calculated VDE of 4.02 eV for the 10-I global minimum from Kappes and co-workers is also in good agreement with the experimental value for the main isomer (Table 1). As can be seen from Table 1, the calculated VDE for the 10B low-lying isomer in both previous studies is in good agreement with the X' isomer. Thus, there is no doubt about the global minimum 10A and the low-lying isomer 10B for Au_{10}^- .

The question now is what are the isomers for X'' and X'''? These two isomers were not recognized in the previous DFT–PES study¹¹ and are only characterized experimentally in the current work under well controlled experimental conditions. As shown in Table 1, the VDE for isomer 10C was calculated to be 3.14 eV in the previous DFT–PES

study,¹¹ in excellent agreement with the VDE of the X'' band (3.12 eV). However, the X''' isomer cannot be assigned to the 3D isomer 10D for two reasons. First, it is much higher in energy and would not be expected to be populated experimentally, in particular under cold conditions. Second, the calculated VDE for isomer 10D is 2.75 eV,¹¹ much lower than the VDE for the X''' isomer (3.49 eV). We suspect that the X''' isomer is due to a hitherto unidentified low-lying planar structure for Au₁₀⁻. According to the current experimental observation, the relative energy of this unidentified X''' isomer should be similar to isomer 10B, *i.e.* it should be more stable than isomer 10C.

IV.2 Isomer-dependent chemical reactivity of Au₁₀⁻ with O₂

Whetten and co-workers showed that the reactivity of Au_n⁻ ($n < 22$) clusters are correlated with the electron affinities of the neutral clusters.⁵ All even-sized clusters with the exception of Au₁₆ have low electron affinities because they are closed shell with a large HOMO–LUMO gap.⁶ In the anions, the extra electron occupies the LUMO of the neutral clusters and is transferred to O₂ in the Au_nO₂⁻ complexes. On the other hand, the odd-sized cluster anions are closed shell with high electron binding energies, which cannot do the electron transfer chemistry to O₂. The exception of Au₁₆⁻ was understood once its unique tetrahedral cage structure was elucidated.²⁰ The neutral Au₁₆ cage has a degenerate HOMO with two unpaired electrons. Thus, it possesses no HOMO–LUMO gap and the extra electron in the Au₁₆⁻ anion enters the partially filled HOMO, resulting in a very large electron binding energy and preventing it from being transferred to O₂. Walter and Hakkinen²¹ used the electron shell model to explain the electronic structure of Au₁₆⁻ and arrived at the same conclusion about its inertness toward O₂.

The situation of the global minimum D_{3h} structure of Au₁₀⁻ is similar to the case of Au₁₆⁻. Because of its high symmetry, it also possesses a partially-filled degenerate HOMO, resulting in its high electron binding energy and its inertness toward O₂. Hakkinen¹² used a 2D-shell model advanced by Lievens and co-workers¹³ to understand the high electron binding energy of the D_{3h} Au₁₀⁻. The current titration experiment and the observation of O₂-physisorption prove unambiguously the inertness of the global minimum D_{3h} Au₁₀⁻ cluster toward O₂. The 10B isomer of Au₁₀⁻ was shown to possess a large HOMO–LUMO gap,¹¹ as also indicated by its low electron binding energy. Thus, this isomer should react with O₂ in similar manner as its neighboring even-sized Au_n⁻ clusters. The electronic structures of isomer X'' and X''' are not known. However, our experiment showed very clearly that they react with O₂, probably in similar fashion as the X' isomer. Thus, not only its size, but also the detailed electronic and atomic structure of a cluster is critical in determining its reactivity. A very small change in structure can have profound effects on the reactivity of a gold cluster. This may be important to be kept in mind when one considers the catalytic mechanisms of supported gold nanoparticles.²²

V. Conclusions

We report a study of the isomers of the Au₁₀⁻ cluster and their reactivity with O₂. Using Ar-tagging and O₂ titration, we have identified at least three low-lying isomers for Au₁₀⁻, in

addition to its D_{3h} global minimum. Two of these isomers (X' and X'') can be assigned according to previous calculations, while one of the isomer with a VDE of 3.49 eV (X''') belongs to a hitherto unidentified Au₁₀⁻ isomer, which should be close in energy with the X' D_{2h} low-lying isomer. All three low-lying isomers were found to react with O₂, whereas the D_{3h} global minimum does not react with O₂ due to its high electron binding energies. The low-lying isomers can be all titrated out of the cluster beam using O₂ to give rise to an essentially isomer-selective beam containing only the global minimum D_{3h} Au₁₀⁻. The isomers and the isomer-dependent chemical reactivity identified for Au₁₀⁻ may be relevant in considering the chemical reactivity of supported gold clusters, where the support may dictate the structures of the clusters and influence their reactivity indirectly.

Acknowledgements

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