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Isomer identification and resolution in small gold clusters

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A variety of experimental techniques are used to resolve energetically close isomers of Au7− and Au8− by combining photoelectron spectroscopy and ab initio calculations. Two structurally distinct isomers are confirmed to exist in the cluster beam for both clusters. Populations of the different isomers in the cluster beam are tuned using Ar-tagging, O2-titration, and isoelectronic atom substitution by Cu and Ag. A new isomer structure is found for Au7−, which consists of a triangular Au6 unit with a dangling Au atom. Isomer-specific photoelectron spectra of Au8− are obtained from O2-titration experiment. The global minimum and low-lying structures of Au7−, Au8−, and MAu8− (n=6,7; M=Ag,Cu) are obtained through basin-hopping global minimum searches. The results demonstrate that the combination of well-designed photoelectron spectroscopy experiments (including Ar-tagging, O2-titration, and isoelectronic substitution) and ab initio calculation is not only powerful for obtaining the electronic and atomic structures of size-selected clusters, but also valuable in resolving structurally and energetically close isomers of nanoclusters. © 2010 American Institute of Physics. [doi:10.1063/1.3299292]

I. INTRODUCTION

The properties of nanoparticles are known to depend on both their size and shape. The discovery of catalytic activities of supported gold nanoparticles1 has stimulated intense interests in the structures and properties of gaseous gold clusters,2−7 which provide atomically defined models for understanding the mechanisms of the catalytic effects of gold nanoparticles.8 Different techniques have been used to probe the structures of gold nanoclusters, including photoelectron spectroscopy (PES),9 ion mobility,10,11 infrared multiphoton dissociation spectroscopy,12,13 and trapped ion electron diffraction.14 While all these techniques are quite powerful, there are deficiencies under certain circumstances. Ar-tagging is especially useful when the isomers have very different structures and, particularly, the isomer issues in a few cases still remain questionable and controversial and need more definitive experimental and theoretical evidence to be resolved.5,13,22,27,31−33

Recently, we have shown that there are at least four coexisting isomers in the Au10− cluster beam31 using Ar-tagging and O2-titration techniques34,35 in combination with PES, revealing the structural diversity and complexity of small gold clusters. We have also observed that planar Au11− clusters, as well as the pyramidal Au20−, have stronger charge-induced intermolecular interactions with Ar, and used this property to obtain isomer-specific PES spectra for Au12− (Ref. 22) and obtained distinct experimental evidence that the cage-to-pyramid crossover occurs at Au18−.28 Although Ar-tagging and O2-titration combined with PES have been proven very useful in resolving isomers of nanoclusters, there are deficiencies under certain circumstances. Ar-tagging is especially useful when the isomers have very different structures, for example, the 2D versus three-dimensional (3D) structures in Au12−.22 If the isomers have similar structures and thus similar charge-induced intermolecular interactions with Ar, it would be difficult to obtain isomer-specific spectra using the Ar-tagging method. O2-titration cannot be used for those clusters unreactive with O2, such as odd-sized Au13− clusters or isomers with similar O2 reactivity. Ion mobility is especially useful in resolving geometrical structures of nanoclusters according to different

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collision cross sections of different isomers. However, just like Ar-tagging, when two isomers have similar structures or similar collision cross sections, it would be very difficult or impossible to resolve the isomers in ion mobility.

In this article, we report a detailed study of the isomers of $\text{Au}_7^-$ and $\text{Au}_6^-$ using Ar and O$_2$-tagging, O$_2$-titration, and isoelectronic atom substitution by Cu and Ag. We show that even for these very small clusters their structural isomers have not been fully understood. Both clusters have been suggested to have multiple isomers in our previous PES study, but not definitively identified. Here we show that there are two energetically and structurally close isomers for each cluster. In particular, we find a dangling Au atom isomer for $\text{Au}_7^-$, which is always populated in the cluster beam but has not been recognized. The relative stability of this isomer is found to vary with Cu or Ag substitution. Using O$_2$-titration, we are able to obtain isomer-specific photoelectron spectrum of $\text{Au}_6^-$. The global minima and the low-lying structures of $\text{Au}_7^-$, $\text{Au}_8^-$, and MAu$_n^-$ ($M=\text{Ag}, \text{Cu}; n=6,7$) are obtained using basin-hopping searches and their computed densities of states (DOS) are used to compare with the PES data.

II. METHODS

A. PES EXPERIMENT

The experiment was carried with a magnetic bottle PES apparatus equipped with a laser vaporization cluster source, details of which has been reported elsewhere. A gold disk target (or a gold target doped with Ag or Cu) 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 perpendicularly into a time-of-flight mass spectrometer. Clusters of interest were selected by a mass gate and attracted perpendicularly into a time-of-flight mass spectrometer. 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 perpendicularly into a time-of-flight mass spectrometer.

B. Theoretical calculations

The structural searches were done using the basin-hopping global minimum search technique coupled with DFT calculations for geometry optimization. Independent searches were performed using basin-hopping programs written by Wei Huang and the University of Nebraska-Lincoln (UNL) group; generalized gradient approximation in the Perdue–Burke–Ernzerhof (PBE) functional form was chosen in both searches. Several randomly selected initial structures were used for the basin-hopping searches, all lead to consistent sets of low-lying isomers for each cluster anion. The top ten lowest-lying isomers were reoptimized using the PBE0/CRENBL hybrid functional/basis set, as implemented in the NWChem 5.1.1 software package. Lastly, relative energies of the top four lowest-lying isomers are computed using the M06-L functional and CRENBL basis set (with inclusion of spin-orbit effects). The results are presented in Figs. S1 and S2 and Tables S1 and S2 of Ref. 47.

III. RESULTS AND DISCUSSION

The photoelectron spectra of $\text{Au}_7^-$ ($n=7,8$) and MAu$_n^-$ ($M=\text{Ag}, \text{Cu}; n=6,7$) along with the corresponding simulated DOS spectra are presented in Figs. 1–4, respectively. The theoretical and experimental VDEs are compared in Table I.

Different anion isomers have different charge-induced intermolecular interactions with Ar. Thus, the relative populations of different isomers can change in the cluster Ar complexes. Figure 1(a) shows that the relative intensities of the second peak ($X'$) and several other peaks in the spectra of $\text{Au}_7$Ar$^-$ (blue curve) are slightly reduced as compared to those of pure $\text{Au}_7^-$ (red curve), indicating that these peaks likely come from a different (minor) isomer, whose interaction with Ar is weaker than that between the major isomer of $\text{Au}_7^-$ and Ar. Furthermore, $\text{Au}_7^-$ does not react with O$_2$. However, we found that O$_2$ can physisorb onto $\text{Au}_7^-$, providing the possibility for O$_2$-tagging. Indeed, we see that the PES spectra of $\text{Au}_7$(O$_2$)$^{2-}$ [Fig. 1(b)] and $\text{Au}_7$Ar$^-$ are very similar. The observed differences between the PES spectra of $\text{Au}_7^-$ and Ar/O$_2$-tagged $\text{Au}_7^-$ are very small; the observation provides experimental hints that there are more than one isomer in the cluster beam.

To provide further evidence about the isomers of $\text{Au}_7^-$, we substituted one Au atom by a Ag or Cu atom. These isoelectronic substitutions can alter the relative stabilities of
the isomers, thereby their relative populations in the cluster beams. Indeed, the PES spectra of AgAu$_6^-$ [Fig. 2(b)] and CuAu$_6^-$ [Fig. 2(c)] show remarkable similarities to that of undoped Au$_7^-$, except that the relative intensities of different peaks are changed. In particular, the relative intensity of the X' peak increased substantially, while those of the X and A peaks decreased. The A peak of AgAu$_6^-$ is overlapped with the A peak [Fig. 2(b)], but it is clear that the relative ratios of the X and A peaks are unchanged, suggesting that they come from one isomer, and this isomer is similar to the main isomer of Au$_7^-$. The X' and A' peaks increased in both the spectra of AgAu$_6^-$ and CuAu$_6^-$ proportionally, and they are similar to the X' and A' peaks in Au$_7^-$, suggesting that this isomer becomes the dominant species in the doped clusters.

To identify the two isomers, we performed basin-hopping global minimum searches combined with DFT calculations on Au$_7^-$, AgAu$_6^-$, and CuAu$_6^-$ from randomly generated initial structures. It should be pointed out that two independent basin-hopping searches$^{36,37}$ on Au$_7^-$ were performed in the current study, one by a program written by one of the coauthors (W. H.) and another by the UNL group. A dangling Au atom isomer of Au$_7^-$ was found independently using both programs. The basin-hopping searches of the Au/Ag and Au/Cu binary clusters were performed solely by the UNL group.$^{38,39}$ The top ten low-lying isomers were re-optimized and relative energies of four low-lying isomers are presented in Fig. S1.$^{47}$ Except CuAu$_6^-$, we found that the 2D planar isomers are appreciably lower in energy than the 3D isomers Fig. S1.$^{47}$ The lowest-energy isomer of CuAu$_6^-$ has a 3D structure. However, the computed DOS spectrum...
Table I. The measured VDEs compared to calculated VDEs for the isomers of the pure gold clusters \( \text{Au}_7^- \) and \( \text{Au}_8^- \), and the doped clusters \( \text{MAu}_8^- \) and \( \text{MAu}_7^- \) (\( M = \text{Ag}, \text{Cu} \)). All energies are in electron volts.

<table>
<thead>
<tr>
<th></th>
<th>Expt. ( ^a )</th>
<th>Theor. ( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Au}_7^- ) (I)</td>
<td>3.46(2) ( ^b )</td>
<td>3.24</td>
</tr>
<tr>
<td>( \text{Au}_7^- ) (II)</td>
<td>3.92(3)</td>
<td>3.61</td>
</tr>
<tr>
<td>( \text{AgAu}_6^- ) (I)</td>
<td>3.45(4)</td>
<td>3.22</td>
</tr>
<tr>
<td>( \text{AgAu}_6^- ) (II)</td>
<td>3.94(3)</td>
<td>3.62</td>
</tr>
<tr>
<td>( \text{CuAu}_6^- ) (I)</td>
<td>3.40(4)</td>
<td>3.24</td>
</tr>
<tr>
<td>( \text{CuAu}_6^- ) (II)</td>
<td>3.94(3)</td>
<td>3.62</td>
</tr>
<tr>
<td>( \text{Au}<em>8^- ) (I, ( \text{D}</em>{3h} ))</td>
<td>2.79(2) ( ^a )</td>
<td>2.69</td>
</tr>
<tr>
<td>( \text{Au}<em>8^- ) (II, ( \text{C}</em>{2v} ))</td>
<td>2.91(4)</td>
<td>2.82</td>
</tr>
<tr>
<td>( \text{AgAu}_7^- ) (I)</td>
<td>2.69(4)</td>
<td>2.61</td>
</tr>
<tr>
<td>( \text{AgAu}_7^- ) (II)</td>
<td>3.06(4)</td>
<td>2.96</td>
</tr>
<tr>
<td>( \text{CuAu}_7^- ) (I)</td>
<td>2.83(4)</td>
<td>2.71</td>
</tr>
<tr>
<td>( \text{CuAu}_7^- ) (II)</td>
<td>3.07(4)</td>
<td>2.97</td>
</tr>
</tbody>
</table>

\( ^a \) Numbers in parentheses represent the uncertainty in the last digit.
\( ^b \) Theoretical VDE is always smaller than the experimental VDE by 0.1–0.3 eV when spin-orbit effects are included in PBE0/CRENBL level calculation.

It is interesting to understand why the difference between the spectra of \( \text{Au}_7^- \) and \( \text{Au}_7\text{Ar}^- \) is small compared to the difference observed previously between the spectra of \( \text{Au}_{12}^- \) and \( \text{Au}_{12}\text{Ar}^- \). This is due to the fact that the two isomers of \( \text{Au}_{12}^- \) are 2D and 3D, respectively, and, therefore, have very different intermolecular interactions with Ar, while both isomers of \( \text{Au}_7^- \) are 2D and have similar intermolecular interactions with Ar.

We also attempted Ar-tagging on \( \text{Au}_8^- \), but the spectra of \( \text{Au}_8\text{Ar}^- \) and \( \text{Au}_8^- \) are nearly identical and cannot be used to distinguish contributions from different isomers. \( \text{Au}_8^- \) is reactive with \( \text{O}_2 \), providing an opportunity to carry out \( \text{O}_2 \)-titration.\(^{27,28}\) We have built a fast flow cluster reactor, which consists of a 25-mm-long and 6 mm diameter stainless steel tube attached to the cluster source nozzle. Reactant gases (\( \text{O}_2 \) here) can be introduced through a hole drilled in the middle of the stainless steel tube. A cap with a 3 mm hole is installed at the exit of the tube to increase the residence time of the reactant. By using a 5% \( \text{O}_2 \)-He reactant gas, we obtained the \( \text{Au}_8^- \) spectrum, as shown in Fig. 3(b). This spectrum is quite different from that using pure He carrier gas (Fig. 3(a)) that we reported previously.\(^{45}\) Specifically, the relative intensities of the \( \text{X}' \), \( \text{A}' \), and \( \text{B}' \) peaks decreased dramatically, suggesting that they come from an isomer that has been titrated out of the cluster beam. The ground state of \( \text{Au}_8^- \) is known to be of a \( \text{D}_{4h} \) structure and its low-lying isomer is a \( \text{C}_{2v} \) structure [Fig. 4(d)].\(^{10,19}\) Clearly, the low-lying \( \text{C}_{2v} \) isomer, which corresponds to the \( \text{X}' \), \( \text{A}' \), and \( \text{B}' \) peaks, is titrated out of the cluster beam. Since Fig. 3(b) contains very little contribution from the \( \text{C}_{2v} \) isomer, this spectrum is subtracted from Fig. 3(a) to yield the isomer-specific spectrum for the \( \text{C}_{2v} \) isomer, as shown in Fig. 3(d).\(^{48}\) The spectrum in Fig. 3(d) is then subtracted from Fig. 3(b) to yield the isomer-specific spectrum for the \( \text{D}_{4h} \) structure [Fig. 3(c)] by appropriate normalization.

The photoelectron spectra of Ag/Cu substituted \( \text{Au}_8^- \) are shown in Figs. 4(b) and 4(c). The peak positions of \( \text{AgAu}_7^- \) and \( \text{CuAu}_7^- \) are almost the same as that of \( \text{Au}_8^- \), suggesting that the same isomers are present in the spectra of the substituted clusters. However, the relative intensities are changed: the \( \text{X}' \), \( \text{A}' \), and \( \text{B}' \) peaks become weaker in the spectrum of \( \text{AgAu}_7^- \) [Fig. 4(b)], implying that the \( \text{C}_{2v} \)-type isomer in \( \text{AgAu}_7^- \) may become less stable. The same peaks become dominant in the spectrum of \( \text{CuAu}_7^- \) [Fig. 4(c)], suggesting that the \( \text{C}_{2v} \)-type isomer may become the global minimum in this system. The weak peak labeled with * in Fig. 4(c) may arise from an unidentified impurity or another minor isomer.
found that the Ag and Cu atoms prefer high coordination sites in AuAg− and CuAu−. The simulated DOS spectra for the two isomers of AuAg− and CuAu− are also in very good agreement with the experimental data, lending additional credence to the structures identified for the substituted clusters. Moreover, the change in the relative stabilities of the isomers of CuAu− [Figs. S2(i) and S2(j)] (Ref. 47) is consistent with the major change in relative populations in the cluster beams as demonstrated by the substantial change in the relative intensity of the X∗ peak versus the X peak [Figs. 4(a) and 4(c)]. However, the change in the relative stabilities of the isomers of AuAg− [Figs. S2(e) and S2(f)] (Ref. 47) is inconsistent with the relatively small change in relative populations in the cluster beams. Perhaps much larger basis sets than the CRENBL or higher-level theories than DFT are needed to resolve this inconsistency.

IV. CONCLUSION

In conclusion, we report a detailed investigation of the structures and isomers of AuAg− and AuCu− using a combination of experimental techniques (Ar-tagging, O2-titration, and isoelectronic substitution) in conjunction with basin-hopping global minimum searches. A new isomer is identified for AuCu−, which consists of a triangular Au6 unit with a terminal Au atom. For AuAg−, we found that O2-titration can be used to titrate out the second lowest-energy isomer to yield isomer−specific PES spectra. The Ag and Cu substituted Au6− and AuCu− clusters are shown to possess similar structures and isomers as the parent clusters and the Ag and Cu dopant atoms are found to prefer high coordination sites. The current study reveals the structural diversity for even relatively small Au clusters and demonstrates that well-designed PES experiments in combination with ab initio calculations are highly valuable to elucidate the structures and energetics of nanoclusters.

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