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Copper doping of small gold cluster cations: Influence on geometric and electronic structure

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The effect of Cu doping on the properties of small gold cluster cations is investigated in a joint experimental and theoretical study. Temperature-dependent Ar tagging of the clusters serves as a structural probe and indicates no significant alteration of the geometry of Au_n^+ ($n = 1\text{--}16$) upon Cu doping. Experimental cluster–argon bond dissociation energies are derived as a function of cluster size from equilibrium mass spectra and are in the 0.10–0.25 eV range. Near-UV and visible light photodissociation spectroscopy is employed in conjunction with time-dependent density functional theory calculations to study the electronic absorption spectra of $\text{Au}_{4-m}\text{Cu}_m^+$ ($m = 0, 1, 2$) and their Ar complexes in the 2.00–3.30 eV range and to assign their fragmentation pathways. The tetramers Au_4^+ , $\text{Au}_4^+ \cdot \text{Ar}$, Au_3Cu^+ , and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ exhibit distinct optical absorption features revealing a pronounced shift of electronic excitations to larger photon energies upon substitution of Au by Cu atoms. The calculated electronic excitation spectra and an analysis of the character of the optical transitions provide detailed insight into the composition-dependent evolution of the electronic structure of the clusters. © 2011 American Institute of Physics. [doi:10.1063/1.3664307]

I. INTRODUCTION

Gold clusters and nanoparticles attracted vast attention during the last 20 years. The fascination for small free or supported gold particles not only originates from their surprising reactivity and catalytic activity¹ but also from their particular geometric and electronic structures.^{2–4} Especially in the non-scalable size regime, ranging from the atom to clusters consisting of about 100 atoms,⁵ the chemical and physical properties of the particles change discontinuously with cluster size opening up new possibilities for the creation of materials with well-defined properties. A new dimension is added when doping clusters with different transition metals, which allows for flexible tuning of the cluster properties, as was demonstrated for doped gold clusters.⁶

Joint ion mobility measurements and density functional theory (DFT) computations revealed the planarity of pure gold cations up to a cluster size of seven atoms,² while they were shown to exhibit 3D structures by substituting one Au atom by Ag or Cr.^{7,8} Nonlinear variations upon gold cluster doping were also observed in electronic properties, such as ionization potentials,⁹ vertical detachment energies,⁹ and charge distributions.^{8,10} Furthermore, photofragmentation studies on a large variety of transition metal doped gold cluster cations provided experimental evidence for dopant induced changes in the electronic shell structure and the number of delocalized electrons.¹¹ Modification of the geometric and electronic structure upon doping is also reflected in

the cluster reactivity. For example, gas-phase studies showed that the reactivity of cationic Au_nAg_m^+ ($n + m = 5, 6$) (Ref. 12) and anionic Au_nAg_m^- ($n + m = 2, 3$) (Ref. 13) toward carbon monoxide and molecular oxygen changes discontinuously with increasing silver content, which is also reflected in considerable differences of the cluster-molecule binding energies.^{12,13}

The optical properties of noble metal nanoparticles attracted a lot of attention,¹⁴ not in the least because their UV-visible absorption spectrum is dominated by the presence of an intense surface plasmon resonance. Classical Mie theory¹⁵ can qualitatively describe the optical response of simple metal particles with a diameter of several nanometers. For smaller clusters, quantum size effects are more important and both collective and molecular excitations can take place.¹⁶ Classical models fail to describe this behavior and semi-quantal models or full *ab initio* approaches are required.^{17,18} The optical response of small noble metal clusters is impacted by the close proximity of filled *d* levels. Because of the large *s-d* separation in Ag atoms, silver clusters are better described by free electron models than gold or copper clusters with a small *s-d* energy separation. Close-lying *d*-electrons are known to quench the oscillator strength by screening the *s* electrons and getting partially involved in the excitations.^{19,20}

Optical absorption spectra of size selected noble metal clusters can be obtained by embedding them in inert gas²¹ or in transparent ceramic matrices.¹⁷ Such matrices prevent the clusters from effectively dissociating upon irradiation and allow using commercially available spectrophotometers. Limitations related to size and shape distributions of the matrix embedded particles can be overcome by spatial modulation far-field optical techniques, permitting optical identification

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of single particles.²² However, the interaction between the clusters and the matrix is not negligible. Direct measurements on clusters in the gas phase do not suffer from interactions with a matrix, but typically the low cluster density in molecular beams prevents direct absorption measurements. Action spectroscopy, i.e., monitoring photon absorption by changes in the clusters themselves instead of changes in the light intensity, is therefore used. Examples are resonant two-photon ionization spectroscopy²³ and photofragmentation, possibly in combination with inert gas tracers. The latter technique was applied by Kappes *et al.* to study the electronic photodissociation spectra of bare charged gold clusters and their rare gas complexes: $\text{Au}_4^+ \cdot \text{Ar}_p$ ($p = 0-4$),²⁴ $\text{Au}_n^+ \cdot \text{Ar}_p$ ($n = 7$; $p = 0-3$ and $n = 8, 9$; $p = 0, 1$),²⁵ and $\text{Au}_n^- \cdot \text{Xe}$ ($n = 7-11$).²⁶

Doping clusters strongly affect the optical properties. While measurements on supported binary gold nanoparticles are reported,²⁷ we are not aware of any experiment on the optical properties of doped gold clusters in the gas phase. Here, we present electronic photodissociation spectra of Cu doped gold cluster tetramers. The influence of Cu doping and of Ar tagging on the optical absorption spectra is analyzed and compared with the results of time-dependent density functional theory calculations (TD-DFT). In addition, temperature-dependent Ar tagging on Au_nCu^+ ($2 \leq n \leq 22$) revealed that the mere substitution of one Au atom by one Cu atom does not significantly change the geometric structure of the clusters.

II. METHODS

A. Experimental setup

Pure and Cu doped gold clusters, Au_n^+ and Au_nCu_m^+ , and their Ar complexes, $\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p$, are simultaneously produced in a dual-target laser vaporization source which is described in detail in Ref. 28. Two independent frequency doubled Nd:YAG lasers vaporize the surface of two translating targets. The injection of a He gas pulse cools the metal vapor and initializes clustering. The clusters are thermalized by heat exchange via the He carrier gas with the walls of the source, which is cooled by a continuous flux of liquid N_2 . A temperature controller allows for stabilization to any temperature in the 80–320 K range. Addition of a small fraction of Ar (1%) to the He carrier gas enables the formation of Ar complexes. After expansion into vacuum, the cluster distribution is skimmed and extracted into a reflectron time-of-flight mass spectrometer (RTOF).

To study the electronic photodissociation spectra of the clusters and their Ar complexes in the near-UV and visible light regime, the cluster beam is exposed to a tunable laser beam within the extraction region of the RTOF. The relative depletion of the clusters and the cluster–argon complexes is measured as a function of the laser photon energy in equidistant steps of 0.01 eV by triggering the photodepletion laser with 5 Hz, while the cluster source and the RTOF are operated at 10 Hz. Thus, for each wavelength, a photodissociation and a reference spectrum are measured simultaneously. Each of these mass spectra represents an accumulation of 2000 cluster production cycles.

The photodissociation experiments are performed in the 2.00–3.30 eV energy range utilizing a Nd:YAG pumped optical parametric oscillator (Quanta-Ray MOPO-PO 1228) equipped with a frequency doubling crystal. The laser wavelengths are calibrated with an external fiber optic spectrometer (Ocean Optics USB4000). Laser pulse energies are measured with a pyroelectric detector before and after the scan of each mass spectrum and are corrected for window transmissions.

B. Data analysis

The photodissociation cross section σ is calculated using the modified Lambert-Beer law²⁴

$$\frac{I}{I_0} = 1 - \alpha + \alpha \exp[-\sigma \Phi]. \quad (1)$$

I/I_0 represents the depletion of the parent ion obtained from the integrated ion intensity in the photodissociation (I) and reference (I_0) mass spectrum, Φ is the photon fluence measured for each wavelength, and α represents an overlap factor accounting for imperfect overlap of the cluster ion beam and the dissociation laser. This overlap factor is estimated to be 0.85 in the 2.00–2.78 eV photon energy range and 0.35 in the 2.76–3.30 eV range. The small α in the high photon energy range originates from the laser beam shape in the frequency doubled mode of the optical parametric oscillator in conjunction with the geometrical configuration of laser and cluster beams. Since the overlap factor cannot directly be measured but must be estimated using geometric arguments, it represents the main source of systematic errors in the computed photodissociation cross section.

Equation (1) assumes that a one-photon process leads to dissociation of the clusters and their Ar complexes. Under the given experimental conditions, the maximal achievable depletion of a certain cluster size does not exceed 40%, which inhibits the measurement of reliable fluence dependencies and, thus, the direct proof of this assumption. However, the low cluster–argon binding energy implies that the dissociation of the $\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}$ complex likely occurs after adsorption of one photon as this leads to excitation into the dissociation continuum of the excited state²⁹ or alternatively fast Ar elimination after internal relaxation into the ground state.³⁰ In contrast, small bare metal clusters exhibit much larger binding energies that impede the direct dissociation from an excited state. Thus, dissociation of bare clusters can be assumed to occur after rapid relaxation of the photo-excited state into the ground state accompanied by conversion of the electronic energy into ground state vibrational energy.³¹ To prove that this process is possible to occur on the time-scale of the present experiment after absorption of one photon, the unimolecular dissociation rate constants k_d of the investigated Au_nCu_m^+ ($n + m = 4$) are calculated according to statistical RRKM (Rice, Ramsperger, Kassel, Marcus) theory^{32,33} by employing the software package MASS KINETICS.³⁴ The required vibrational frequencies and the bond dissociation energies of Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ are taken from our theoretical computations performed for the minimum energy structures. For modeling the transition state, the vibrational frequencies are taken to be the same as for the ground state structures

FIG. 1. Unimolecular dissociation rate constants as a function of the photon energy for different photodissociation pathways of Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ at 203 K calculated by employing the RRKM theory.

minus the middle frequency that is treated as internal translation along the reaction coordinate, and two neighboring frequencies are scaled by a factor of 0.5.¹³ Figure 1 displays the calculated unimolecular dissociation rate constants k_d as a function of the applied laser photon energy for different dissociation pathways of Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ (at $T = 203$ K). Due to the small size of the investigated clusters and their small number of available vibrational degrees of freedom, the unimolecular dissociation is much faster (typical 1–1000 ps) than the time-scale of our experiment (few tens of μs). Thus, the photodissociation process is very likely to occur upon absorption of a single photon, and multi-photon processes can be neglected for the small clusters. Schweizer *et al.* came to a similar conclusion for the photodissociation process of Au_4^+ following an analysis of the fluence dependencies.²⁴ Consequently, the experimental photodissociation spectra are regarded as photoabsorption spectra and can be directly compared with the theoretically obtained electronic excitation spectra.

C. Theoretical methods

The optical absorption of the four-atom clusters is modeled using a two step process. In the first step, the cluster geometries are optimized with DFT (Ref. 35) employing the B3LYP hybrid functional³⁶ and the Aug-cc-pVTZ-PP basis sets.³⁷ The structures are searched in such a way that all the possible combinations of Au, Cu, and Ar atoms are considered. A frequency analysis is performed to confirm that all optimized structures are local minima on the potential energy surface. These local minima are then used in the second step, which employs the time-dependent density functional method at the B3LYP/Aug-cc-pVDZ-PP level to calculate the energies and oscillator strengths of the transitions from the ground electronic state to excited electronic states. The optical transitions are combinations of several electronic transitions between a pair of molecular orbitals. Each of these electronic transitions has a statistical weight and contributes with a certain portion to an overall optical transition. The theoretical

FIG. 2. Total fraction F_{Ar} of formed gold-argon $\text{Au}_n^+ \cdot \text{Ar}_p$ and gold-copper-argon $\text{Au}_{n-1}\text{Cu}^+ \cdot \text{Ar}_p$ complexes at (a) 297 K, (b) 203 K, and (c) 158 K, calculated according to Eq. (2).

photodissociation cross sections are obtained from the computed oscillator strengths by modeling the transitions as a sum of Gaussian peaks. The integrals of the Gaussians are linearly proportional to the oscillator strength and the full width at half maximum was chosen to be 60 meV, which represents the value of the smooth (non-structured) peak in the experimental spectra of Au_3Cu^+ .

III. RESULTS AND DISCUSSION

A. Temperature-dependent formation of cluster-van der Waals complexes

1. Geometrical structure of copper doped gold clusters

The likelihood for Ar attachment to small gas-phase clusters is associated with the surface structure of the cluster.³⁸ Recently, the physisorption of Ar on clusters proved to be a successful structural probe for (1) the transition from exohedrally to endohedrally doped clusters,³⁹ as well as for (2) the geometrical transition from 2D to 3D structures and the determination of cluster sizes with pronounced plane faces of monoatomic species.^{4,26} In the latter case, the geometry dependence of rare gas attachment is attributed to differences in the induced dipole interaction between the rare gas atom and 3D structures (interaction potential $\sim R^{-6}$) and flat surfaces ($\sim R^{-3}$), in conjunction with a significant drop in the cluster polarizability at the structural 2D $\rightarrow$ 3D transition due to a decrease in the electron delocalization volume per atom in more compact 3D structures.^{19,40}

Figure 2 displays the total fraction of argon-complexes F_{Ar} of Au_n^+ and $\text{Au}_{n-1}\text{Cu}^+$ formed at cluster source

temperatures of 297 K (trace a), 203 K (trace b), and 158 K (trace c). F_{Ar} is calculated as

$$F_{\text{Ar}} = \frac{\sum_{p=1}^{p_{\text{max}}} I(\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p)}{\sum_{p=0}^{p_{\text{max}}} I(\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p)} \quad (2)$$

with $I(\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p)$ representing the integrated ion intensities of the corresponding mass peaks. At room temperature (Fig. 2(a)), only Au^+ , the dimers Au_2^+ and AuCu^+ , as well as the trimers Au_3^+ and Au_2Cu^+ attach one Ar atom, while no stable $\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p$ complexes for $(n+m) \geq 4$ are observed. Cooling the cluster source considerably enhances the Ar attachment. At 203 K, the small Au_n^+ clusters adsorb up to three Ar atoms and exhibit a strong size dependence in the Ar complex formation (Fig. 2(b)). The Ar complex formation is easier on the odd sized clusters Au_3^+ and Au_5^+ than on the even sized clusters Au_2^+ , Au_4^+ , and Au_6^+ . Further cooling of the source to 158 K (Fig. 2(c)) reduces this odd-even staggering, but a distinct drop in F_{Ar} appears after Au_7^+ . Surprisingly, F_{Ar} is strongly enhanced for $\text{Au}_{10}^+/\text{Au}_{11}^+$ and Au_{15}^+ compared to their neighbors.

In the present experiment on the gold cations, a distinct drop in the Ar attachment is observed after Au_7^+ (Figs. 2(b) and 2(c)), which exactly corresponds to the 2D $\rightarrow$ 3D transition that occurs at $\text{Au}_7^+ \rightarrow \text{Au}_8^+$.² The remarkable large F_{Ar} for Au_{10}^+ , Au_{11}^+ , and Au_{15}^+ can most likely be attributed to almost planar faces of the Au_{10}^+ quasi-tetrahedral structure, the fairly open prismatic structure of Au_{11}^+ ,^{2,41} and the layered structure of Au_{15}^+ .⁴² The pronounced odd-even oscillation of F_{Ar} at small cluster sizes stays elusive. These odd-even variations might be a consequence of differences in the interaction between the Ar atom and the dipole moment of the Au atoms in the cluster. For a detailed understanding of this behavior, comprehensive high-level theoretical calculations are necessary, which go beyond the scope of this paper.

Figure 2 also presents the fraction of Ar complexes for singly doped $\text{Au}_{n-1}\text{Cu}^+$. Although the maximum number of attached Ar atoms does not exceed two for the doped clusters, F_{Ar} shows similar cluster size-dependent features as for pure Au_n^+ : (i) odd-even oscillation of F_{Ar} with enhanced Ar complex formation for odd sized (i.e., an odd number of atoms) Au_2Cu^+ and Au_4Cu^+ ; (ii) distinct drop in the Ar clustering after the seven atom cluster Au_6Cu^+ , which is already pronounced at $T = 203$ K; and (iii) enhanced Ar attachment for $\text{Au}_9\text{Cu}^+/\text{Au}_{10}\text{Cu}^+$ and $\text{Au}_{14}\text{Cu}^+$. Such similarities in the size dependence of the F_{Ar} values for pure and singly copper doped gold clusters indicate that the isoelectronic Cu for Au substitution in the cationic clusters does not significantly alter the geometric structure and the critical cluster size for the 2D $\rightarrow$ 3D structural transition. This finding is consistent with previous photofragmentation experiments on $\text{Au}_{n-1}\text{Cu}^+$ yielding equivalent stability patterns as Au_n^+ , which already indicated a nearly unaltered geometrical structure upon Cu doping.⁴³ On the other hand, a recent photoelectron spectroscopy study on anionic clusters demonstrated a shift of the 2D $\rightarrow$ 3D structural transition from Au_{12}^- to $\text{Au}_{10}M^-$ upon isoelectronic substitution with $M = \text{Cu}$ and Ag .⁴⁴ Also calculations on neutral Au_{n-1}Cu using the semi-empirical Gupta potential and a genetic algorithm

FIG. 3. Van't Hoff plot for $\text{Au}_4^+ \cdot \text{Ar}$ and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$. The slope of the linear fits yields $-\Delta H^0$, which equals the binding energy of the Ar atom to the cluster cations.

predicted a considerable change in the geometry by the mere substitution of Au by Cu. However, semi-empirical calculations are known to less accurately describe the geometry of small clusters.⁴⁵

2. Experimental argon binding energies

To interpret the electronic photodissociation experiments of the Ar complexes, quantitative knowledge of the Ar binding energies is useful. High-level calculations for the atomic gold and copper cations yielded binding energies of 0.27–0.46 eV (Au^+) and 0.19–0.52 eV (Cu^+) depending on the level of theory and the employed basis set.⁴⁶ On the other hand, theoretical predictions for Ar binding on gold or copper clusters are scarce since the weak interactions due to dispersion forces are poorly described by DFT methods.⁴⁷ Therefore, experimentally obtained binding energies are indispensable.

A common technique to determine reaction enthalpies and entropies and thus to compute binding energies of neutral atoms/molecules to a metal cluster ion is the analysis of temperature-dependent equilibrium mass spectra. Under the assumption of equilibrium between the clusters and their Ar complexes in the thermalization room of the cluster source, which is frozen out afterwards, experimental equilibrium constants K_{eq}^0 can be determined from the integrated intensities of the corresponding clusters in the mass spectra.³⁹ The equilibrium constants K_{eq}^0 are then used to calculate the enthalpy ΔH^0 and entropy change ΔS^0 of the reactions in their standard state

$$\ln(K_{\text{eq}}^0) = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R}. \quad (3)$$

Since ΔH^0 is, to a good approximation, temperature independent in the investigated temperature range, the plot of the experimental K_{eq}^0 values versus the inverse temperature $1/T$ (van't Hoff plot) allows for the determination of $-\Delta H^0$ which is equivalent to the cluster–argon binding energy E_0 . As an example, Fig. 3 displays the van't Hoff plots of $\text{Au}_4^+ \cdot \text{Ar}$

TABLE I. Experimentally obtained binding energies (in eV) of the p th Ar atom to gold and gold-copper cluster cations, respectively.

$\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p$	$p = 1$	$p = 2$	$p = 3$
$\text{Au}_2^+ \cdot \text{Ar}_p$	0.10 ± 0.03	0.22 ± 0.03	
$\text{Au}_3^+ \cdot \text{Ar}_p$	0.22 ± 0.02	0.21 ± 0.03	0.25 ± 0.03
$\text{Au}_4^+ \cdot \text{Ar}_p$	0.20 ± 0.02	0.19 ± 0.02	0.19 ± 0.03
$\text{Au}_5^+ \cdot \text{Ar}_p$	0.20 ± 0.03	0.17 ± 0.02	0.20 ± 0.03
$\text{Au}_6^+ \cdot \text{Ar}_p$	0.21 ± 0.03		
$\text{Au}_2\text{Cu}^+ \cdot \text{Ar}_p$	0.17 ± 0.03	0.25 ± 0.02	
$\text{Au}_3\text{Cu}^+ \cdot \text{Ar}_p$	0.26 ± 0.02		

and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$. It is apparent that the equilibrium constant increases (i.e., the formation of Ar complexes is enhanced) with decreasing temperature indicating a barrier-free Ar adsorption on the cluster.⁴⁸ Similar temperature dependencies are observed for all investigated Ar complexes $\text{Au}_n\text{Cu}_m^+ \cdot \text{Ar}_p$ and the resulting binding energies are summarized in Table I. The error bars on the binding energies originate from the fit quality, since systematic uncertainties in the determination of the partial Ar pressure do not affect the slope of the fit curve and, thus, the resulting binding energy.

The experimentally obtained binding energies of a first attached Ar atom to the bare gold cations range between 0.10 ± 0.03 eV and 0.22 ± 0.02 eV. The experimental $\text{Au}_4^+ \cdot \text{Ar}$ binding energy amounts to 0.20 ± 0.02 eV, while the theoretical value, obtained with the present B3LYP calculations, is 0.14 eV. Previous studies for Ar on Au_4^+ , at the DFT (B3LYP) and RI-MP2 level of theory, gave binding energies of 0.12 eV and 0.21 eV, respectively.^{24,25}

Due to the rather small temperature dependence of Ar attachment for some Cu doped gold cations, the determination of reliable binding energies was only possible for $\text{Au}_2\text{Cu}^+ \cdot \text{Ar}_p$ ($p = 1, 2$) and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$, which amounts to 0.17 ± 0.03 eV, 0.25 ± 0.02 eV, and 0.26 ± 0.02 eV, respectively. The calculated value for $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ is 0.22 eV, also slightly underestimating the strength of the cluster bond with argon. It is striking that the Ar binding energy on Au_3Cu^+ (0.26 ± 0.02 eV) is slightly larger than on Au_4^+ (0.20 ± 0.02 eV). The DFT calculations show that in $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$, the Ar atom preferably binds to the Cu atom. The larger Au_3Cu^+ -Ar bond strength can then be attributed to the following two effects: (i) The Cu atom in Au_3Cu^+ is more positively charged than the Au atoms, resulting in a larger dipole moment and, thus, a stronger bond with the neutral argon atom by instantaneous dipole-induced dipole interaction. (ii) The London dispersion interaction is inversely proportional to R^6 , with R the bond distance between Cu or Au and Ar. The atomic radius of Cu (1.45 Å),⁴⁹ leading to a much smaller bond distance of 2.46 Å compared to 2.79 Å for $\text{Au}_4^+ \cdot \text{Ar}$ [Table II] and, thus, an enlarged binding energy.

B. Experimental and theoretical photodissociation spectra

The interpretation of photodissociation spectra of bare metal clusters is complicated by the fact that a certain cluster

TABLE II. Calculated interatomic distances d (in Å) of the minimum-energy isomers of Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ and their Ar complexes. The structures are optimized at the B3LYP/Aug-cc-pVTZ-PP level. The labeling of the atoms is given in Figs. 4–8.

$\text{Au}_{4-m}\text{Cu}_m^+ \cdot \text{Ar}_p$	d	
$\text{Au}_4^+ (\text{D}_{2h})$	Au1–Au2	2.699
	Au1–Au3	2.728
	Au1–Au4	2.712
$\text{Au}_4^+ \cdot \text{Ar} (\text{C}_{2v})$	Au1–Au2	2.687
	Au1–Au3	2.712
	Au2–Au3	2.722
$\text{Au}_3\text{Cu}^+ (\text{C}_{2v})$	Au1–Ar	2.788
	Au1–Au2	2.661
	Au1–Cu3	2.581
$\text{Au}_3\text{Cu}^+ \cdot \text{Ar} (\text{C}_{2v})$	Au2–Cu3	2.541
	Au1–Au2	2.647
	Au1–Cu3	2.581
$\text{Au}_2\text{Cu}_2^+ (\text{D}_{2h})$	Au2–Cu3	2.574
	Cu3–Ar	2.458
	Cu1–Au2	2.490
$\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2 (\text{D}_{2h})$	Cu1–Cu3	2.515
	Cu1–Au2	2.493
	Cu1–Cu3	2.560
	Cu2–Ar	2.540

can be both source and product of a photodissociation process, which might lead to complex photodissociation spectra when several dissociation channels overlap. This problem can be overcome by studying Ar complexes instead of bare clusters as long as it is assumed that (1) the optical excitation of an Ar complex leads to the elimination of the Ar atom only and (2) the rare gas atom interacts only weakly with the cluster and does not strongly perturb the optical properties. Earlier photodissociation studies on gold cations revealed a small change in the photoabsorption spectra upon Ar attachment.^{24,25} However, photodissociation measurements on neutral Cu_3 exhibited a significant alteration of the spectra upon Ar attachment.⁵⁰ Consequently, it is worthwhile not only to investigate the Ar complexes but, if possible, also the bare clusters in order to assign the influence of the Ar atom.

To avoid overlapping dissociation channels, the experimental conditions are optimized to have only one Ar atom attached to the cluster size of interest, Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ . Thus, the parameters of the cluster source are tuned for maximum production of the tetramers and the temperature of the cluster source is fixed at 203 K. Under these experimental conditions, Au_4^+ , $\text{Au}_4^+ \cdot \text{Ar}$, Au_3Cu^+ , and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ are present in sufficient amount, whereas Au_2Cu_2^+ as well as $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}$ are not observed. Instead, the attachment of two Ar atoms is preferred on Au_2Cu_2^+ , yielding $\text{Au}_2\text{Cu}_2^{2+} \cdot \text{Ar}_2$.

In Secs. III B 1–III B 5, the experimental photodissociation spectra together with calculated electronic excitation spectra of the tetramers and their Ar complexes are presented. Hereto, the experimental photodissociation cross sections are derived using Eq. (1). The calculated TD-DFT excitation spectra are presented without energy correction or scaling factors. Geometric details of the ground state Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ structures as well as their Ar complexes are given in Table II. Experimental peak positions and oscil-

TABLE III. Peak positions (in eV) and oscillator strengths of the experimentally observed optical transitions of the investigated cluster tetramers and their Ar complexes. The oscillator strength is derived according to $f = 0.91103 \cdot \int \sigma(E) dE$.^{24,54}

	Peak	Peak position	Oscillator strength f
Au_4^+	I	2.45–2.70	0.038
	II	3.02–3.28	0.027
$\text{Au}_4^+ \cdot \text{Ar}$	I	2.70	0.061
	II	3.02–3.17	0.015
Au_3Cu^+	I	2.98	0.045–0.053
	II	≥ 3.23	> 0.007
$\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$	I	≥ 3.10	> 0.078

lator strengths are summarized in Table III, and electronic transitions of the ground state Au_3Cu^+ and Au_2Cu_2^+ structures are given in Tables IV and V.

1. Bare gold tetramers Au_4^+ and $\text{Au}_4^+ \cdot \text{Ar}$

Figures 4(a) and 4(c) display the experimental photodissociation spectra of Au_4^+ and its Ar complex, $\text{Au}_4^+ \cdot \text{Ar}$. Au_4^+ exhibits two distinct peaks at 2.60 eV (peak I) and 3.21 eV (peak II) with relatively small photodissociation cross sections of about $0.4 \text{ \AA}^2$. Both peaks are broad and have underlying structures. The photodissociation spectrum of the argon complex, $\text{Au}_4^+ \cdot \text{Ar}$, is slightly different. The main peak (I) is blueshifted by 0.1 eV (2.70 eV) and has a width (FWHM) of 75 meV, much narrower than the corresponding feature of Au_4^+ . The cross section is enhanced by a factor of 1.9. A second broader peak (II) is observed in the photon energy range of 3.01–3.17 eV.

The absorption of one photon by Au_4^+ fragments the cluster under monomer elimination. Alternative fragmentation channels yielding Au_2^+ or Au^+ are not observed. This finding is in accord with previous photodissociation experiments demonstrating the preferred monomer evaporation of Au_4^+ .^{24,51} The Ar binding energy is determined to be $0.20 \pm 0.02 \text{ eV}$, while for Au_4^+ the dissociation energy for

monomer loss was calculated to be 1.36 eV. Although the dissociation of the Ar complex under the mere loss of the Ar atom is expected, the fragmentation under a combined elimination of Ar and one Au atom yielding Au_3^+ as product cannot be excluded from energetic considerations.

In agreement with previous studies,^{2,41,48,52} the minimum energy structure of the bare gold tetramer and its Ar complex is found to be a rhombic D_{2h} structure with the Ar atom attached to a threefold coordinated gold atom. The ground state structures and the computed excitation spectra are shown in Figs. 4(b) and 4(d). Both calculated excitation spectra satisfactorily describe the main characteristics of the experimental spectrum with the major peak labeled C corresponding to feature I. However, the position of the bands are shifted in energy by about 0.22–0.24 eV. Excitation spectra of other isomers are not considered in the present work but were discussed in Ref. 24.

Our experimental and theoretical photodissociation spectra of Au_4^+ and $\text{Au}_4^+ \cdot \text{Ar}$ are in favorable agreement with a previous study by Kappes *et al.*²⁴ The position and shape of peak I of Au_4^+ and $\text{Au}_4^+ \cdot \text{Ar}$ as well as of peak II of $\text{Au}_4^+ \cdot \text{Ar}$ are exactly reproduced. Peak II of Au_4^+ is slightly blueshifted in the present experiment and its structure is more pronounced, which may be due to a larger density of data points in this wavelength region. Further, low intensity transitions at 2.25 eV and 2.40 eV (Au_4^+) as well as 2.21 eV and 2.43 eV ($\text{Au}_4^+ \cdot \text{Ar}$) with photodissociation cross sections of $\sigma \leq 0.1 \text{ \AA}^2$ were not resolved under the present experimental conditions. Compared to the previous study, the absolute cross sections derived in the present experiment are slightly larger but within the estimated error bars. In particular, the relative cross sections of peaks I and II differ by less than 15%.

2. Au_3Cu^+

The photodissociation spectrum of Au_3Cu^+ is shown in Fig. 5(a). The spectrum is dominated by one major peak at 2.98 eV (peak I). In contrast to the broad and structured features in the Au_4^+ spectrum, it is structureless and exhibits a

TABLE IV. Electronic transitions of Au_3Cu^+ ground-state structure iso 1 (symmetry, transition energy, and oscillator strength) obtained at the B3LYP/Aug-cc-pVDZ-PP level, initial and final MOs participating in these transitions with $\geq 5\%$, as well as percentage of total s -, p -, d -type character of the initial and final orbitals. MO excitations contributing $\geq 40\%$ to the electronic transitions are listed in bold.

Excitation	Initial orbitals	Final orbitals	s -/ p -/ d -Contribution to	
			Initial orbitals	Final orbitals
A (B_2 , 3.04 eV, 0.073)	11B₂ α	17A₁ α	76/13/11	93/5/2
	10A₁ β	11B₂ β	13/2/85	76/9/15
B (B_2 , 3.09 eV, 0.019)	9B ₂ α	16A ₁ α		
	10A ₁ β	11B ₂ β		
	9B₂ β	16A₁ β	13/2/85	89/5/6
C (B_2 , 3.23 eV, 0.1152)	9B ₂ α	16A ₁ α		
	11B ₂ α	17A ₁ α		
	10A₁ β	11B₂ β	13/2/85	76/9/15
	9B ₂ β	16A ₁ β		
D (B_2 , 3.40 eV, 0.0086)	9B₂ α	16A₁ α	8/2/90	89/6/5
	9B₂ β	16A₁ β	13/2/85	89/5/6

TABLE V. Electronic transitions of Au_2Cu_2^+ ground-state structure iso 1 (symmetry, transition energy, and oscillator strength) obtained at the B3LYP/Aug-cc-pVDZ-PP level, initial and final MOs participating in these transitions with $\geq 5\%$, as well as percentage of total s -, p -, d -type character of the initial and final orbitals. MO excitations contributing $\geq 40\%$ to the electronic transitions are listed in bold.

Excitation	Initial orbitals	Final orbitals	s - p - d -Contribution to	
			Initial orbitals	Final orbitals
A (B_{1u} , 3.28 eV, 0.1416)	$7B_{1u} \alpha$	$10A_g \alpha$	75/7/18	91/6/3
	$5A_g \beta$	$7B_{1u} \beta$		
B (B_{1u} , 3.48 eV, 0.0143)	$4B_{3g} \alpha$	$7B_{2u} \alpha$	0/0/100	86/6/8
	$7B_{1u} \alpha$	$10A_g \alpha$		

width (FWHM) of only 60 meV. A second peak arises at the blue end of the wavelength range with an onset at 3.23 eV (peak II).

The binary tetramer Au_3Cu^+ is observed to fragment into Au_2Cu^+ under elimination of one Au atom. An alternative fragmentation channel yielding Au_3^+ under elimination of the Cu atom cannot be completely excluded on the basis of the experimental data. However, the calculated RRKM dissociation rate constants for Au loss are considerably larger than for Cu loss [cf. Fig. 1], indicating Au loss as preferred reaction channel on the basis of statistical considerations. The dimer elimination is not observed in the experiment and the sequential loss of Cu and Ar can be precluded from energetic considerations.

The calculations reveal as minimum energy structure of Au_3Cu^+ a rhombus (C_{2v} symmetry) with the Cu atom located at a three-fold coordinated position [iso 1 in Fig. 5(b)] and slightly contracted bond distances compared to the most stable rhombic isomer of the pure Au_4^+ [cf. Table II]. A rhombic isomer with the Cu atom on a two-fold coordinated position [iso 3 in Fig. 5(d)] is 0.31 eV higher in energy. In addition, three stable isomers of (partially distorted) Y-shape are found. Of these three, the lowest energy isomer structures

[iso 2 in Fig. 5(c)] (0.25 eV higher in energy than the ground state structure) has a strongly distorted Y-shape (C_s symmetry) with the Cu atom located on one of the two-fold coordinated edges of the triangle. The remaining isomers [iso 4 and iso 5 in Figs. 5(e) and 5(f)] are nearly isoenergetic (0.41 eV and 0.42 eV, respectively). Iso 4 has the Cu atom located on the long side of the non-distorted Y and exhibits C_{2v} symmetry, while the Cu atom in iso 5 is located on the three-fold coordinated middle position of a distorted Y (C_s symmetry). These geometries and their energetic ordering are in favorable agreement with a previous DFT study⁵³ on Au_nCu_m^+ . Merely, the geometries of iso 4 and iso 5 differ from the

FIG. 4. Left: Experimental photodissociation spectra of (a) Au_4^+ and (c) $\text{Au}_4^+ \cdot \text{Ar}$. The open circles represent the experimental data points, while the solid red lines are obtained by averaging over five adjacent data points. The experimental cross sections are determined according to Eq. (1) by assuming a one-photon process. Right: Corresponding electronic excitation spectra for the ground state structures. The minimum energy D_{2h} and C_{2v} structures, respectively, are shown as insets in (b) and (d). The sticks represent the oscillator strength as obtained from the TD-DFT calculations, while the curves represent calculated photodissociation cross sections.

FIG. 5. Comparison of (a) the experimental photodissociation spectrum of Au_3Cu^+ with (b)–(f) calculated electronic excitation spectra of five energetically low-lying isomers. The open circles represent the experimental data, while the solid red line in (a) is obtained by averaging over five adjacent data points. Experimental cross sections are determined according to Eq. (1) by assuming a one-photon process. Isomeric structures, point group symmetries, and energy differences with respect to the most stable cluster are displayed as insets.

previous ones, which predicted iso 4 to be distorted and 0.06 eV higher in energy than the non-distorted iso 5.

Figures 5(b)–5(f) also display the calculated excitation spectra for the different isomeric structures exhibiting several distinct features in the relevant energy range. By comparison with the experimental photodissociation spectrum, it is obvious that the experimental data cannot be explained by the calculated spectra of iso 3 and iso 5, which exhibit optical transitions at too low and too high energies, respectively. In contrast, under consideration of the finding for Au_4^+ and $\text{Au}_4^+ \cdot \text{Ar}$ that the theoretical excitations tend to be slightly blueshifted, the spectra of iso 1, iso 2, and iso 4 might roughly describe the experimentally observed peak at 2.98 eV and the onset of a second peak at the blue edge of the spectrum. Thus, on the basis of this photodissociation spectrum alone, the unambiguous assignment of a structural motif is not possible. Furthermore, the theoretical cross sections are found to generally overestimate the experimentally obtained ones in agreement with the previous studies.^{24,26} However, the Ar attachment experiments presented in Sec. III A, indicate that the geometry of the cluster does not significantly change upon doping with one copper atom which is also confirmed by the present DFT calculations predicting the rhombic iso 1 as minimum energy structure. Based on these experiments, it is assumed that most probably iso 1 represents the cluster present in the beam. The preference of iso 1 is further supported by the experimental and theoretical spectra of $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ as will be discussed next.

3. $\text{Au}_3\text{Cu} \cdot \text{Ar}^+$

Adding one Ar atom to Au_3Cu^+ further shifts the optical absorption spectrum to higher photon energies (Fig. 6(a)). While in case of the pure gold tetramer the shift upon Ar attachment of the main peak amounts to only 0.1 eV, already the onset of the high energy $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ peak I is shifted by as much as 0.2 eV. Furthermore, this peak is strongly broadened and exhibits a distinct underlying structure pointing to several transitions occurring in a relatively small energy range.

It is expected that $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ fragments under elimination of the Ar atom. However, the main peak I apparent for $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ is not reflected as an increased signal in the spectrum of Au_3Cu^+ where it should appear as a flop-out signal. This indicates that $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ does not fragment by the mere loss of the Ar atom but an alternative fragmentation channel that corresponds to the joint loss of the Ar atom and one metal atom is observed. Such a process is feasible at photon energies larger than the cluster dissociation energy, since the liberation of the weakly bound Ar atom yields a vibrationally highly excited Au_3Cu^+ species that can further dissociate unimolecularly. Indeed, the fragmentation of $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ under the joint elimination of Ar and one Au atom is experimentally observed, while there is no experimental evidence for the loss of a Cu atom. The preference of this fragmentation path over the alternative channel leading to Ar and Cu loss is in agreement with the calculated RRKM dissociation rate constants as can be seen from Fig. 1. In the photon energy range of the observed optical tran-

FIG. 6. Comparison of (a) the experimental photodissociation spectrum of $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ with (b)–(g) calculated electronic excitation spectra of six isomers comprising a rhombic structure of the cluster core. The open circles represent the experimental data, while the solid red line in (a) is obtained by averaging over five adjacent data points. Experimental cross sections are determined according to Eq. (1) by assuming a one-photon process. Isomeric structures, point group symmetries, and energy differences with respect to the most stable cluster are displayed as insets.

sitions for $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$, the rate for Au loss is about 20 times larger than the rate for Cu loss, which is a consequence of the lower Au binding energy ($E_0(\text{Au}-\text{Au}_2\text{Cu}^+) = 1.41$ eV compared to $E_0(\text{Au}_3^+-\text{Cu}) = 1.96$ eV) and the larger reaction path degeneracy.³³

Since the DFT calculations indicated a rhombic structural motif for Au_3Cu^+ , Figs. 6(b)–6(g) display only isomeric structures of $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ based on the two rhombic cluster cores found for bare Au_3Cu^+ with the Cu atom either located on a three-fold or two-fold coordinated position. Attaching Ar to the lowest energy isomer of Au_3Cu^+ (iso 1 in Fig. 5(b)) yields three stable configurations that are all within a 0.11 eV energy range (Figs. 6(b)–6(d)). The three possible Ar complexes of the second rhombic Au_3Cu^+ isomer [iso 3 in Fig. 5(d)] are considerably higher in energy.

Comparison of the corresponding excitation spectra with the experimental data reveals a favorable agreement of iso 1 (Fig. 6(b)) with the experimental photodissociation spectra. Peak I of the experimental spectrum can be assigned to features A–C of the calculated spectrum. In contrast, the spectra of iso 2–6 do not reconcile with the measurements. Iso 2,

FIG. 7. (a)–(e) Calculated electronic excitation spectra for different isomeric structures of Au_2Cu_2^+ . This cluster was not formed under the present experimental conditions.

3, and 5 exhibit peaks that are located at too low energies, while iso 4 and 6 reveal only one major transition at energies ≥ 3.2 eV and, thus, do not resemble the broad structured experimentally observed peak I. In addition, none of the Y-shaped isomers is able to reproduce the experimental spectrum (not shown on figure).

4. Au_2Cu_2^+

As mentioned above, the bare cluster Au_2Cu_2^+ was not formed under the present experimental conditions and can, thus, only be discussed in terms of theoretical calculations. Figure 7 displays five low-lying stable isomers and their corresponding electronic excitation spectra. The most stable isomer (iso 1) exhibits a rhombic structure with the Cu atoms occupying the two three-fold coordinated positions. The second-lowest isomer iso 2 (+0.34 eV) is also a rhombus with two Cu atoms located at a two- and a three-fold coordinated position, respectively. A strongly distorted Y-shaped motif (iso 3) is found 0.40 eV above the ground state, followed by two non-distorted Y-shaped isomers at 0.54 eV (iso 4) and 0.80 eV (iso 5). These isomeric structures as well as their energetic ordering are in excellent agreement with a previous study on Au_nCu_m^+ .⁵³ Especially, the large energy difference between the lowest energy iso 1 and the first Y-shaped iso 3 indicates that even the substitution of two Au atoms by two Cu atoms does not significantly alter the geometry.

The electronic excitation spectrum of the ground state iso 1 exhibits one dominant transition at 3.28 eV. In contrast, iso 2–iso 4 reveal several transitions in the 2.8–3.3 eV energy range. Similar to the ground state iso 1, the excitation spec-

FIG. 8. (a)–(c) Calculated electronic excitation spectra of three isomeric structures of $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$ based on the minimum energy structure of bare Au_2Cu_2^+ . No electronic transitions are experimentally found in the investigated photon energy range.

trum of iso 5 only shows transitions at the high energy edge of the investigated region.

5. $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$

The easy physisorption of two Ar atoms on Au_2Cu_2^+ yields the complex $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$ for which no electronic transition is observed in the investigated photon energy range of 2.00–3.30 eV. This either implies a lack of electronic excitations in the investigated energy range or that the electronic excitations have dissociation cross sections smaller than the detection limit. Figures 8(a)–8(c) display the geometric structure and corresponding excitation spectra of three isomers based on the rhombic cluster core of the minimum energy structure of Au_2Cu_2^+ (Fig. 7(a)). All three isomers lie in a small energy range of 0.18 eV and exhibit distinct peaks at energies ≥ 3.2 eV. The main peaks for iso 2 and 3 correspond to energies of 3.41 eV and 3.56 eV (labeled B and C in Figs. 8(b) and 8(c), respectively) and, thus, are outside the investigated photon energy range, which favorably explains the lack of peaks in the experimental spectrum. In contrast, iso 1 reveals two peaks at 3.23 eV and 3.33 eV (labeled B and C in Fig. 8(a)), which should at least be partly recognizable in the experiment. However, iso 1 cannot completely be excluded as a structural motif since it is likely to assume a coexistence of all three isomeric structures due to their close energetic spacing which in turn might considerably reduce the detection limit of feature B in the iso 1 excitation spectrum.

6. Composition dependence

The calculated electronic excitation spectrum of the lowest energy isomer of Au_4^+ (Fig. 4(b)) is dominated by four transitions, while the spectra of ground-state isomers of Au_3Cu^+ (Fig. 5(b)) and Au_2Cu_2^+ (Fig. 7(a)) comprise only two and one major peak(s), respectively. Furthermore, the dominant transitions are blueshifted with increasing Cu content in agreement with the experimental findings.

FIG. 9. Density of electronic states (DOS) profiles of Au_4^+ (dotted black curve), Au_3Cu^+ (dashed red curve), and Au_2Cu_2^+ (solid green curve). Spin-up MOs are labeled α_1 – α_6 , while spin-down MOs are labeled β_1 – β_6 . The horizontal line indicates the separation between occupied and unoccupied states. The vertical arrows illustrate transitions mainly contributing to the observed overall electronic transitions.

Each electronic transition can be considered as a joint excitation involving several one-electron molecular orbitals (MOs). The decomposition of the electronic excitations in the 2.0–3.5 eV range of Au_3Cu^+ and Au_2Cu_2^+ are presented in Tables IV and V. The decomposition of the electronic excitations of the ground state isomer of Au_4^+ agrees with the results presented in Ref. 24 and is not discussed here. The angular momentum decomposition of the MOs reveals that all observed transitions occur between initial MOs having strong *d* and *s* character and final MOs having strong *s* character resulting in electronic excitations predominantly involving $d \rightarrow s$ and $s \rightarrow s$ transitions. Transitions involving MOs of strong *p* character are not observed in the investigated photon energy range. This finding is in agreement with theoretical optical absorption spectra of neutral gold clusters indicating a considerable involvement of *d* electrons in low-energy transitions due to a strong *s*–*d* hybridization in the molecular orbitals of Au_n clusters.¹⁹

To further analyze the optical transitions and in particular the change in the electronic structure of the clusters upon Cu doping, Fig. 9 displays the density of electronic states (DOS) profiles of Au_4^+ (dotted black curve), Au_3Cu^+ (dashed red curve), and Au_2Cu_2^+ (solid green curve). The overall electronic spectra of all three clusters show very similar features. Due to the atomic configuration of Au ($5d^{10} 6s^1$) and Cu ($3d^{10} 4s^1$) resulting in one unpaired electron in the cationic tetramers, the DOS profiles of spin-down levels are characterized by a high density of MOs with dominating *d* character (labeled β_3 in Fig. 9) located close to the highest occupied molecular orbital (HOMO) and *s*-type MOs (β_4) located close to the lowest unoccupied molecular orbital (LUMO). In contrast, the DOS profiles of spin-up levels exhibit *s*-type MOs (α_4 and α_5) in the vicinity of both the HOMO and the LUMO. Upon Cu for Au substitution in the cluster, the occupied spin-up MOs labeled α_3 (*d* character) shift to higher

energy, while the α_4 HOMO (*s* character) shift to lower energy reducing the energetic difference between *d*-type and *s*-type occupied MOs which can be attributed to a smaller *s*–*d* atomic orbital separation in the Cu atom (0.5 eV) compared to the Au atom (1.1 eV). Furthermore, the unoccupied MOs α_5 and α_6 are considerably destabilized resulting in an increased spin-up α_4 – α_5 gap (2.20 eV, 2.65 eV, and 3.25 eV for Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ , respectively). For the spin-down states, the occupied β_3 and unoccupied β_5/β_6 MOs shift to higher energies, while the unoccupied β_4 MO hardly shifts upon Cu doping yielding a slightly reduced spin-down β_3 – β_4 gap (2.66 eV, 2.45 eV, and 2.29 eV for Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ , respectively). The overall HOMO–LUMO gap increases from 1.34 eV (Au_4^+) to 1.39 eV (Au_3Cu^+) and 1.51 eV (Au_2Cu_2^+).

The major electronic excitations in the investigated photon energy range of 1.8 eV–3.6 eV can be mainly assigned to $\alpha_3 \rightarrow \alpha_5$, $\alpha_4 \rightarrow \alpha_6$, $\beta_3 \rightarrow \beta_4$, and $\beta_3 \rightarrow \beta_5$ transitions as indicated by the arrows in Fig. 9. The observed general trend of a blueshift in these excitations with increasing Cu content in the cluster is in agreement with the significant destabilization of the unoccupied β_5 , α_5 , and α_6 MOs in conjunction with the stabilization of the occupied α_4 MO.

7. Effect of Ar complex formation

The calculated minimum energy structures of the four-atomic Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ clusters and their Ar complexes show that the adsorption of one or two Ar atoms hardly perturbs their planar rhombic structure (bond length change by less than 2%, cf. Table II). Changes in the energetic ordering of the lowest energetic isomers upon Ar physisorption are not likely because of the rather small Ar binding energies. Despite the negligible influence of the Ar atom on the geometric structure, significant differences are observed in the photodissociation spectra: (1) The dominating Au_4^+ peak I is blueshifted by 0.1 eV and its structure disappears upon Ar adsorption; (2) Peak I of Au_3Cu^+ becomes broad and structured in $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ and its onset is blueshifted by as much as 0.2 eV. These differences are also reflected in the theoretical electronic excitation spectra.

In a previous study on $\text{Au}_4^+ \cdot \text{Ar}$, the effect of Ar on the optical transitions was theoretically studied in detail revealing significant changes in the peak positions and the oscillator strength for Ar adsorption on the short axis (three-fold coordinated Au atom) of Au_4^+ . Similarly striking differences in the electronic excitation spectra merely caused by the adsorption site of the Ar atom are also observed for the binary tetramer $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$. The adsorption of Ar on a two-fold coordinated atom slightly blueshifts the dominant transitions, while the overall features hardly change (compare, e.g., iso 1 in Fig. 5(b) with iso 3 in Fig. 6(d)). In contrast, attachment of Ar to a three-fold coordinated atom strongly perturbs the excitation spectra (compare, e.g., iso 1 in Fig. 5(b) with iso 1 and iso 2 in Figs. 6(b) and 6(c)). For facile comparison, transitions in the excitation spectra of bare clusters and their Ar complexes (Figs. 4–8) involving similar initial and final molecular orbitals are labeled with identical letters.

FIG. 10. Density of electronic states (DOS) profile of Au_3Cu^+ (dashed red curve) and its Ar complexes $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ iso 1 (dotted black curve) and iso 3 (solid green curve). Spin-up MOs are labeled α_1 – α_6 , while spin-down MOs are labeled β_1 – β_6 . The horizontal line indicates the separation between occupied and unoccupied states. The vertical arrows illustrate transitions mainly contributing to the observed overall electronic transitions.

To illustrate the effect of Ar physisorption on the cluster electronic structure and to elucidate the changes in the photodissociation and electronic excitation spectra dependent on the adsorption site of Ar, Fig. 10 compares the DOS profiles of Au_3Cu^+ (dashed red curve) with $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ iso 1 (dotted black curve) and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ iso 3 (solid green curve). From these curves, it is obvious that Ar attachment does not change the overall features of the DOS in a wide energy range; merely additional states arise at the low and high energy edges of the spectrum. However, Ar adsorption causes a shift of the occupied MOs α_1 – α_4 and β_1 – β_3 to higher energies by about 0.2–0.3 eV, while the unoccupied MOs α_5 , α_6 , and β_4 – β_6 are destabilized by about 0.2–0.5 eV. The netto effect yields a slightly increased spin-up α_4 – α_5 gap and a decreased spin-down β_3 – β_4 gap. The enlarged spin-up α_4 – α_5 gap causes higher excitation energies of transitions exhibiting high spin-up MOs contribution. Furthermore, Fig. 10 reveals that among the MOs participating in the investigated electronic transitions (indicated by vertical arrows), mainly the unoccupied MOs α_5 and β_5 are affected by the adsorption site of the Ar atom on the cluster. These MOs are considerably more destabilized for the $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$ iso 1 than for iso 3 in agreement with the experimentally observed strong shift of the main transition upon Cu doping.

Similar destabilization effects of all MOs are also observed for $\text{Au}_4^+/\text{Au}_4^+ \cdot \text{Ar}$ and $\text{Au}_2\text{Cu}_2^+/\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$, though the shift in the energetic location of the MOs is slightly smaller for $\text{Au}_4^+ \cdot \text{Ar}$ but significantly larger for $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$. The less pronounced perturbation of the Au_4^+ electronic structure arises from the somewhat weaker interaction between the Ar atom and Au_4^+ ($E_0 = 0.20 \pm 0.02$ eV) compared to Au_3Cu^+ ($E_0 = 0.26 \pm 0.02$ eV). In contrast, the enhanced destabilization of the $\text{Au}_2\text{Cu}_2^+ \cdot \text{Ar}_2$ MOs is the result of the simultaneous binding of two Ar atoms on Au_2Cu_2^+ .

Thus, it can be concluded that Ar physisorption only changes the overall electronic structure of the clusters to a minor extent, although the photodissociation and electronic excitations spectra might be strongly influenced, in particular for systems exhibiting rather strong cluster–rare gas interaction. Consequently, for analysis of the experimental data and direct comparison with theoretical computations, the consideration of the rare gas atom is indispensable and, if possible, van der Waals effects should be included explicitly.

IV. SUMMARY

In this contribution, we presented a joint experimental and theoretical investigation elucidating changes in the geometric and electronic structure of small gold clusters upon copper doping. Ar physisorption was used as a structural probe for the geometric 2D $\rightarrow$ 3D transition and the determination of cluster sizes with striking plane faces of gold cations and singly copper doped gold cations. Identical size-dependent Ar physisorption behavior of Au_n^+ and $\text{Au}_{n-1}\text{Cu}^+$ indicates very similar structural motifs, confirming previous experimental studies.

Furthermore, near-UV and visible light photodissociation spectroscopy on Au_nCu_m^+ ($n + m = 2$ –4) and their Ar complexes was performed. Their fragmentation pathways are assigned and electronic transitions in the employed energy range of 2.00–3.30 eV were observed for Au_4^+ , $\text{Au}_4^+ \cdot \text{Ar}$, Au_3Cu^+ , and $\text{Au}_3\text{Cu}^+ \cdot \text{Ar}$. Corresponding time-dependent density functional theory calculations allow for the assignment of the rhombic minimum energy structure as a structural motif for the tetramers Au_4^+ , Au_3Cu^+ , and Au_2Cu_2^+ . The observed transitions are found to arise from joint excitations of several electrons from one-electron molecular orbitals predominantly involving $d \rightarrow s$ and $s \rightarrow s$ transitions. Although the photodissociation and electronic excitation spectra exhibit marked blueshifts of the transitions with increasing copper content, the overall electronic structure of the clusters reveals very similar features.

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