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H. Handschuh, Gerd Ganteför, P. S. Bechthold, Wolfgang Eberhardt

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A comparison of photoelectron spectroscopy and two-photon ionization spectroscopy: Excited states of Au_2, Au_3, and Au_4

H. Handschuh, G. Ganteför, P. S. Bechthold, and W. Eberhardt

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Photoelectron spectra of Au_n^- with $n = 2-4$ are reported. Due to the relatively high photon energy used in our experiment ($h\nu = 6.424$ eV) and the energy resolution of about 50 meV, various transitions into excited states of the neutral clusters are resolved. It is demonstrated that photoelectron spectra can serve as a map of the electronic states of a cluster, while the high resolution of the resonant two-photon ionization (R2PI) method gains information about the symmetry of the states. The comparison with similar data of Ag_n^- clusters indicates the influence of relativistic effects and the large spin–orbit splitting for Au.

I. INTRODUCTION

Photoelectron spectroscopy of metal and semiconductor cluster anions[1-10] has been proven to be a valuable tool for the study of the electronic and geometric structure of such particles. The spectroscopy of anions exhibits two major advantages compared to electron spectroscopy of neutral species: (1) the charged clusters can be mass separated by conventional methods; and (2) the spectra contain direct information about the ground and excited electronic states of the neutral cluster. Compared to resonant two-photon ionization[11-13] (R2PI), which yields high resolution spectra of certain excited states of dimers and trimers, photoelectron spectroscopy on anions [PES(A)] can serve as a guide to map the multitude of electronic states of a neutral particle.

As a first example for the comparison with R2PI experiments, we present here PES(A) spectra of Au_2^-, Au_3^-, and Au_4^- recorded with an energy resolution[14] sufficient to resolve details of the electronic structure of these particles. The group I b metal (Cu,Ag,Au) clusters exhibit a certain similarity to the alkali clusters. The s-derived electronic orbitals are delocalized and therefore an electronic shell structure[10] can be observed as described by the electronic shell model.[15] In contrast, the d-derived orbitals[3] are localized and the mass dependence of this part of the density of states in the cluster cannot be described by a simple model. For all three group I b bulk metals,[4,16] the uppermost electronic orbitals within ≈ 2 eV of the highest occupied molecular orbital (HOMO) are s derived. The d-derived orbitals[16] of Ag exhibit an about 2 eV higher binding energy (BE) than Cu and Au and therefore, Ag clusters should resemble the closest similarity to alkali clusters concerning the electronic structure close to the HOMO. By comparison with Au and Cu data, the effects of $s-d$ hybridization can be studied.[10]

For Au clusters, the electronic structure[11,12,17-29] is complicated by two effects: (1) the BE of the $6s$ derived orbitals is enhanced by relativistic effects. This results, e.g., in an enhanced bond strength, smaller bond lengths, and an about 0.5–1 eV higher electron affinity as compared to Ag and Cu. (2) the $5d$ derived orbitals exhibit a large spin–orbit splitting, which even exceeds the $5d$ "bandwidth" for the smaller clusters resulting in separated $D_{5/2}$ and $D_{3/2}$ derived manifolds of orbitals. Therefore, the PES(A) spectra of small Au_n^-

clusters[2,4] do not show an obvious similarity with the data of Cu_n^- and Ag_n^- clusters.[1-4,10,30] Also, very few theoretical data[17-29] are available for Au clusters because of the difficulty to include the localized d-derived orbitals, the large spin–orbit interaction, and the relativistic effects into the calculations. In the present contribution, we try to understand the spectra of the very small Au clusters by comparison with the available data. The PES(A) study will be extended to larger clusters up to $n = 20$ in a subsequent paper.[31]

II. EXPERIMENTAL SETUP

PES(A) suffers from the problem of the extremely low target density present in an ion beam. Therefore, especially at photon energies higher than the work function of the surrounding metal surfaces (≈ 5 eV), it is difficult to achieve a reasonable signal to noise ratio at sufficient energy resolution. With our recently designed new electron spectrometer,[14] we improved both the signal to noise ratio and the energy resolution to record PES(A) spectra of a quality sufficient for a comparison with R2PI data.

The electron spectrometer is described in detail elsewhere.[14] Gold cluster anions are generated by a laser vaporization source. The metal anions are extracted from the He supersonic jet and mass separated by a time-of-flight mass spectrometer. A bunch of clusters of a certain size is irradiated by an UV laser light pulse (ArF excimer laser $h\nu = 6.424$ eV). The kinetic energy of the detached electrons is determined using a "magnetic bottle" time-of-flight electron spectrometer.[32]

The energy resolution[14] of the spectrometer depends sensitively on the velocity distribution of the incoming anions. The spectrometer collects almost all electrons emitted into the 4π solid angle. The Doppler effect due to the ion velocities smears out the electron kinetic energies. To improve the energy resolution, the anions are decelerated by a pulsed electric field just prior to the detachment. Caused by the Doppler effect, the energy resolution increases with increasing mass of the clusters and increasing BE. The upper limits are about $\Delta E = 0.15$ eV at 2 eV BE and $\Delta E = 40$ meV at 5 eV BE for the atom. With increasing particle size, this broadening decreases as a function of the anion velocity. The spectrometer is energy calibrated using the known BEs of the
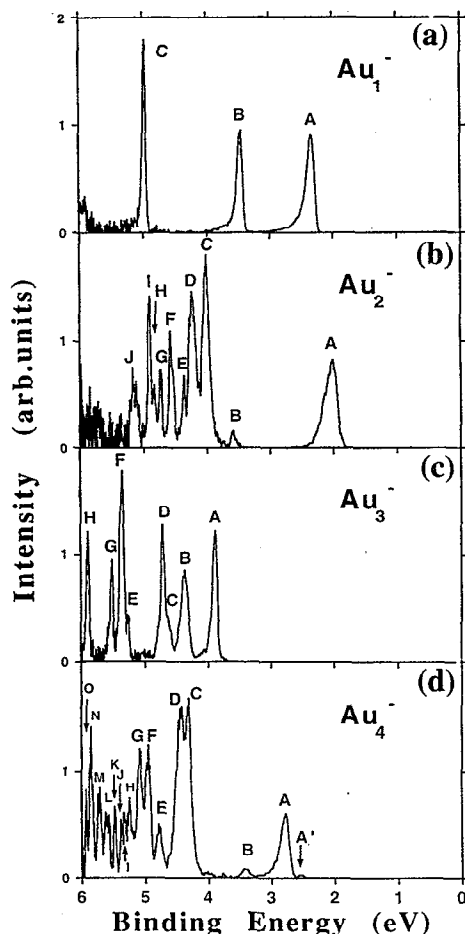
FIG. 1. PES(A) spectra of Au⁻, Au₂⁻, Au₃⁻, and Au₄⁻ taken at $h\nu = 6.424$ eV photon energy (ArF excimer laser). Feature A is assigned to the transition from the electronic ground state of the anion into the electronic ground state of the neutral particle. The assignments of the marked peaks are discussed in the text.

features observed in the PES(A) spectrum of Au₁⁻ [Fig. 1(a)]. The absolute measured value of the BE of a peak exhibits an estimated systematic error of ±25 meV due to residual electrostatic potentials within the spectrometer. However, the difference in BE between two peaks can be measured more accurately. The uncertainty of a difference in the BE of two peaks is estimated to decrease linearly with decreasing energy separation with a maximum value of ±25 meV at 6 eV energy difference.

III. RESULTS

Figures 1(a)–1(d) display photoelectron spectra of Au_n^- clusters with $n = 1-4$. The three features observed in the PES(A) of Au_1^- correspond to transitions from the anion electronic ground state $^1S_0$ into the neutral ground state $^2S_{1/2}$ [Fig. 1(a), peak A] and the excited states $^2D_{5/2}$ (peak B) and $^2D_{3/2}$ (peak C) of the neutral atom.[2] The BE of the ground state transition[2] is equal to the electron affinity of Au [=2.309 eV (Ref. 33)], while the BEs of two excited states ($^2D_{5/2} = 3.445$ eV, $^2D_{3/2} = 4.967$ eV) can be calculated as

TABLE I. Positions and widths of the peaks displayed in Fig. 1. The positions correspond to the binding energy (BE) of the maximum of a feature. The uncertainty of the BE is ±25 meV. The width equals the FWHM and represents a convolution of the experimental resolution and the widths of the Franck–Condon distribution. The uncertainty of the width is ±30%. All values are given in electron volts.

Peak	Au₂⁻ Position	Au₂⁻ Width	Au₃⁻ Position	Au₃⁻ Width	Au₄⁻ Position	Au₄⁻ Width
A′					2.54	0.07
A	2.01	0.23	3.89	0.08	2.78	0.15
B	3.60	0.07	4.38	0.15	3.42	0.13
C	4.02	0.14	4.62	0.10	4.32	0.10
D	4.25	0.15	4.73	0.07	4.44	0.14
E	4.38	0.05	5.28	0.07	4.79	0.12
F	4.59	0.07	5.36	0.07	4.95	0.12
G	4.75	0.05	5.53	0.05	5.10	0.11
H	4.85	0.05	5.90	0.05	5.26	0.07
I	4.92	0.05			5.34	0.05
J	5.15	0.15			5.37	0.05
K					5.49	0.04
L					5.62	0.09
M					5.74	0.07
N					5.85	0.05
O					5.93	0.04

the sum of the electron affinity and the excitation energies of the two states [$^2D_{5/2} = 1.136$ eV (Ref. 34), $^2D_{3/2} = 2.658$ eV (Ref. 34)].

Table I presents the peak positions and widths as extracted from the spectra of Au₂⁻, Au₃⁻ and Au₄⁻ displayed in Fig. 1. The shape of a peak represents a convolution of the experimental resolution and the Franck–Condon profile of the corresponding electronic transition. In most cases, the widths are nearly equivalent to the experimental resolution and therefore the determination of the true width of the Franck–Condon distribution is difficult. In cases where the width of a transition is much larger than the width of a neighboring peak, this corresponds either to a broad Franck–Condon distribution or to the overlap of more than one electronic transitions hidden in the broad feature.

The peaks located at the lowest BE (Fig. 1, marked A) correspond to the transitions from the anion electronic ground states into the neutral electronic ground states. The BEs of these features are equal to the vertical detachment energy (VDE)[1–3,5] of the clusters. This is the energy corresponding to the transition from the electronic and vibrational ground states of the anion into the electronic ground state of the neutral with the nuclei fixed at the positions of the anion ground state. The vertical electron affinity (VEA) on the contrary corresponds to the transition from the neutral electronic ground state into the electronic ground state of the anion with the geometry of the neutral. In most cases, the geometry of the anion differs from the geometry of the neutral. Because the geometries involved into the two processes discussed here (electron attachment, electron detachment) are different,[1,2,35] the two energies (VDE and VEA) are different.

Weak features in the PES(A) spectra are difficult to assign due to the possibility of various background effects giving rise to additional peaks in the spectra (e.g., peak B in the

spectrum of Au_2^- and feature A' in the spectrum of Au_4^-). In some cases, we observed weak features in the PES(A) spectra which were assigned to transitions from an excited electronic state of the anion (e.g., $Al_2^-{}^*$),[35] although the anions are cooled in a supersonic expansion. Another possibility of additional features in the spectra are impurities (e.g., hydrides and oxides), which are not completely separated from the bunch of the bare metal clusters due to the limited mass resolution of the time-of-flight mass spectrometer. However, no contaminations could be identified in the mass spectrum of Au_n^-.

IV. BASIC MODELS

In R2PI spectroscopy,[11–13] neutral particles in the electronic ground state are excited using laser radiation (e.g., of a dye laser) with a tunable photon energy. A second laser with fixed photon energy, usually operating in the UV, serves to ionize the excited molecules. The intensity of the ions is recorded as a function of the photon energy of the tunable laser. The spectra exhibit peaks at photon energies corresponding to optical transitions from the neutral ground state into electronically excited states of the neutral particle. Only dipole allowed transitions can be observed. However, in systems with strong spin–orbit coupling such as Au, even singlet–triplet transitions are not totally forbidden due to the breakdown of the spin–orbit coupling.

In PES(A), the detachment energies of the electrons are measured corresponding to transitions from the ground state of the anion into various electronic configurations of the neutral system in the geometry of the anion. The Franck–Condon profile of a peak depends on the difference in geometry between the initial state and the final state of the corresponding transition. The position of a peak (=maximum of intensity) is the energy of the vertical transition. Because the initial state in PES(A) spectra is usually the ground state of the anion, the observed Franck–Condon profiles are generally different from the ones measured in R2PI experiments. In cases where the ground state geometries of the anion and the neutral cluster differ strongly, the comparison of R2PI spectra and PES(A) spectra is difficult due to the possible shifts of the peak positions.

In principle, the vertical excitation energies of the excited electronic states of the neutral particle with respect to the neutral ground state can be extracted from the PES(A) spectra. This energy corresponds to the difference between the VDE and the BE of the peak corresponding to the transition from the anion ground state into the neutral excited state. One has to take into account, however, that the vertical transition energies might be different from the ones measured in R2PI due to the differences in the Franck–Condon profiles.

While the maxima of the Franck–Condon profiles are located at different energies (both measured with respect to the neutral ground state) for the two methods, the positions of individual vibrational transitions are fixed: the energy spacing between two certain vibrational levels of neutral electronic states measured by the two methods are equal. If the vibrational structure of a transition is resolved and as-signed, both methods deliver basically identical information about the neutral states. However, only in a few cases, vibrational resolution[1,2,6,7,9,35] has been achieved in PES(A).

Excited states of neutral metal clusters can also be studied by matrix spectroscopy,[36–39] i.e., photoabsorption and fluorescence. However, for the very small particles studied here, the matrix induced shifts are large compared to the spacings between the electronic transitions and depend on the symmetry of the involved electronic states and trapping sites.[39] Therefore, for an assignment of features observed in matrix spectra to peaks in the PES(A) spectra, a careful analysis of these shifts is necessary.

From a comparison of R2PI spectroscopy and photo-depletion on neutral alkali clusters, it has been argued[13] that R2PI fails to detect certain excited states in clusters larger than the dimer due to the very short lifetimes of these excited states. The lifetime of the electronically excited states decreases with increasing cluster size due to the increasing density of states associated with an increase in the number of relaxation pathways. Whether this is the real reason or not has to be decided yet. The fact is, however, that from the manifold of excited states found in our PES(A) spectra of Au clusters, about $\approx 50\%$ of the dimer but none of the trimer and tetramer states have been detected using R2PI spectroscopy. In the case of the trimer, only a quartet state[12] (corresponding to a doublet–quartet transition) has been detected by R2PI, which cannot be measured by PES(A) due to the different selection rules (see below).

V. DISCUSSION

A. Au_2^-

Our PES(A) data of Au_2^- [Fig. 1(a) and Table I] can be compared to the results of R2PI experiments[11] and to the results of calculations[17–22] on the neutral dimer. To do so, the energy scale has to be calibrated to the neutral ground state. The vertical detachment energy (VDE) (position of the maximum of peak A) has to be subtracted from the BEs of the peaks corresponding to transitions into excited states. Table II displays the excitation energies of the excited states of Au_2 resulting from this calculation. Also included in Table II are the corresponding excitation energies (positions of the 0–0 vibrational transitions) found in R2PI studies.[11]

According to Table II, all five excited states found in R2PI spectroscopy[11] correspond to peaks in the PES(A) spectrum displayed in Fig. 1 (peaks C, D, E, I, and J) located at nearly the same excitation energy. Additional features are observed (peaks B, F, G, and H) in the PES(A) spectrum, which can be explained by the less restrictive selection rules related to the emission of an electron. That is, optical transitions from the neutral ground state into these excited states seem to be dipole forbidden.

The excitation energies extracted from the PES(A) spectrum are in all cases slightly smaller than the R2PI values (between 10 and 70 meV). In the R2PI experiment, the energies of the 0–0 vibrational transitions are generally assigned in the spectra. These energies are per definition equal to the adiabatic excitation energies. As discussed above, due to the lack of vibrational resolution in PES(A), only the ver-

TABLE II. A comparison of the excitation energies of the excited states of Au_2 as extracted from the PES(A) spectrum [Fig. 1(a)] with the corresponding R2PI data (Ref. 11). In the case of PES(A), the excitation energy is calculated as the difference of the measured BE of a transition into an excited state of the neutral dimer from the VDE (taken as the position of peak $A = 2.01$ eV). In the case of R2PI, the excitation energies (Ref. 11) are the measured positions of the 0–0 vibrational transitions from the neutral ground state into the excited electronic states. All values are given in electron volts. The uncertainty of the differences of the measured BEs is ± 15 meV.

| | Experimental excitation energy | | |
Peak	PES(A)	R2PI[a]	Notation[a]
A	0.00	0.00	$X\ ^1\Sigma_g^+$
B	1.59		
C	2.01	2.06	$a\ ^3\Sigma_u^+$
D	2.24	2.25	$A'\ 1_u$
E	2.37	2.43	$A\ 0_u^+$
F	2.58		
G	2.74		
H	2.84		
I	2.91	2.98	$B'\ (1_u?)$
J	3.14	3.18	$B\ 0_u^+$

[a]Reference 11.

tical transition energies (VTEs) can be determined as differences between the VTEs (peak maxima) into the neutral ground and the excited states. The VTEs differ from the adiabatic transition energies depending on the differences in equilibrium bond lengths between the electronic ground state of the anion and the neutral ground and the excited states.

In the case of Au_2, the electronic ground state of the neutral dimer exhibits a shorter bond length than the neutral excited states and the anion ground state. The two $6s$ electrons of the neutral dimer occupy the bonding σ orbital. The bond length of the anion ground state is larger because the additional electron occupies the antibinding σ^* orbital. Generally, the bond lengths of the excited states of the neutral dimer are also longer because all observed states [Fig. 1(b)] correspond most likely to single electron–hole excitations of an electron into the antibinding σ^* orbital (see below). Therefore, the bond lengths of the anion ground state and the neutral excited states are similar, but the one of the neutral ground state is relatively short. Accordingly, the Franck–Condon profiles of the transitions from the anion ground state into the neutral excited states [Fig. 1(b) peaks $C–J$] exhibit smaller widths than the transition into the neutral ground state (peak A). However, the width of peak A is also enlarged due to the lower energy resolution of the spectrometer for electrons with higher kinetic energies, and an unambiguous determination of the peak width is not possible.

The VTE into the neutral ground state ($=$VDE) is enlarged due to the relatively large difference in geometry. Only transitions into higher vibrational levels exhibit a considerable intensity according to the Franck–Condon principle. Due to this effect, the BE of the transition into the neutral ground state (peak $A = 2.01$ eV) is enlarged by about 70 meV. The position of the 0–0 vibrational transition of peak A is equal to the adiabatic electron affinity and is 1.94 eV.[2,6] In contrast, the energy difference between the 0–0 vi-

brational transitions and the observed peak maxima is expected to be smaller for all other peaks due to the similar bond lengths. Because the excitation energies of the neutral dimer are extracted from the PES(A) spectrum by subtraction of the BE of peak A from the BEs of the peaks corresponding to transitions into the neutral excited states, all values of the excitation energies are too small. The differences vary between 10 and 70 meV due to the remaining differences in bond lengths between the excited neutral states.

An unambiguous assignment of the PES(A) peaks to the R2PI features is possible (Table II) because the changes in the measured excitation energies corresponding to the differences in the Franck–Condon profiles between R2PI and PES(A) data are relatively small.

A qualitative understanding of the PES(A) spectrum of Au_2^- can be gained by comparison with the results of calculations.[17–22] However, due to the large spin–orbit interaction in Au, the electronic states of the dimer are determined by Hund's case c, which makes a description difficult. The low lying electronic states of the dimer can be classified into four groups.[11,19,22] Each group of states corresponds to a combination of certain electronic states in the separated atom limit: (1) ^2S and ^2S; (2) ^2S and $^2D_{5/2}$; (3) $^2D_{5/2}$ and $^2D_{5/2}$; (4) ^2S and $^2D_{3/2}$.

The two separated Au atoms in their electronic ground states (^2S and ^2S) give rise to only two low lying electronic states of the dimer. These can be reasonably well described in terms of Hund's case a. The electronic ground state $X\ ^1\Sigma_g^+(5d_A^{10}5d_B^{10}\sigma_g^2)$ and the first excited state $a\ ^3\Sigma_u^+(5d_A^{10}5d_B^{10}\sigma_g^1\sigma_u^{*1})$ (marked A and C, respectively). The optical transition into this state corresponds to an excitation of one of the $6s$ bonding electrons (occupying the σ_g orbital) into the antibinding σ_u^* orbital.

Due to the large spin–orbit splitting in the Au atom (1.522 eV), the electronic states derived from $^2S/^2D_{5/2}$ atoms are lower in energy and clearly separated from the $^2S/^2D_{3/2}$ derived states. We can exclude $^2D_{5/2}/^2D_{5/2}$ derived states from the discussion if we assume that the transitions observed in the PES(A) spectrum correspond to single electron processes. That is, the final state has a configuration almost equal to the configuration of the anion with one electron missing. The $^2D_{5/2}/^2D_{5/2}$ derived states correspond to the simultaneous excitation of two d electrons (shake-up processes) and within this approximation they might be neglected.

According to the above considerations, we tentatively assign the low lying excited states in the PES(A) spectrum except for the $X\ ^1\Sigma_g^+$ and the $a\ ^3\Sigma_u^+$ states to transitions into excited states of the neutral Au dimer derived from $^2S/^2D_{5/2}$ combined Au atoms only. Indeed, the peaks C, D and I assigned in the R2PI studies[11] belong to the $^2S/^2D_{5/2}$ derived manifold of states. The $B\ 0_u^+$ state (peak J) is assigned to a $^2S/^2D_{3/2}$ derived state.[11] However, compared to the other $^2S/^2D_{3/2}$ derived states, its bond strength is drastically enhanced by mixing with an ion pair state[11] of Au_2 ($Au^+ + Au^-$). Due to this mixing, this excited state is lowered in excitation energy towards the upper edge of the $^2S/^2D_{5/2}$ derived manifold of states in agreement with our PES(A) spectrum.

The lack of features beyond peak J [Fig. 1(b)] at high BEs corresponds to the gap between $^2S/^2D_{5/2}$ and $^2S/^2D_{3/2}$ derived states. Calculations[19,22] predict a low bond strength for all $^2S/^2D_{3/2}$ derived states (except for the B 0_u^+ state) compared to the bond strengths of the $^2S/^2D_{5/2}$ manifold of states. Though the centers of the two manifolds of states are in principle separated by ≈ 1.5 eV only, the low bond strengths of the states belonging to the $^2S/^2D_{3/2}$ manifold enhances the energy spacing between the two manifolds. Despite the considerable width of each manifold they are separated by a gap.

A low resolution PES(A) spectrum[4] taken at $h\nu = 7.9$ eV displays three intense peaks located between 6–7 eV BE, beyond the gap. This observation confirms the above consideration of a gap between 5.3 and 6 eV BE in agreement with the calculations.[19,22]

Using a simple picture a photoelectron spectrum reflects the occupied single particle orbitals within a particle. This picture is qualitatively correct if the configurations of the final states of the features observed in a spectrum differ from the configuration of the initial state (=the ground state of the anion) only by the removal of a single electron. The kinetic energy of the emitted electron can be calculated as the difference of the photon energy and the BE of the single particle orbital. Within this framework, the PES(A) spectrum is a qualitative picture of the configuration of the ground state of the anion. Peak A [Fig. 1(b)] corresponds to photoemission from the antibonding $6s$-derived σ^* orbital (occupied by the additional electron of the anion), and peak C corresponds to the bonding $6s$-derived σ orbital (occupied by two electrons). In terms of solid state physics, the manifold of features corresponding to the removal of a single electron out of a $6s$- or $5d_{5/2}$-derived single particle molecular orbital is called the $6s$ or $5d_{5/2}$ "band." Accordingly, features A and C correspond to photoemission from the $6s$ band, while features D–I reflect the $5d_{5/2}$ band of the dimer anion. The features[4] observed beyond 6 eV BE are assigned to the $5d_{3/2}$ band of the cluster anion. In the dimer, the two spin–orbit components of the $5d$ band of Au are still separated. With increasing cluster size, the two subbands are expected to broaden further and the gap will vanish.

The experimental results[11] and the theoretical data[17–22] agree with the a $^3\Sigma_u^+$ state (peak C) as the first excited state of Au_2. Therefore, feature B (Fig. 1 and Table II) cannot be assigned to a transition from the anion ground state into an excited state of the neutral dimer. There are three possible effects giving rise to additional peaks in the PES(A) spectra:

1. Fragmentation

The photoabsorption process can also result in fragmentation[2] of the dimer anion into Au^- and Au. A second photon can detach the electron from Au^-. According to this multiphoton process, features belonging to the PES(A) spectrum of Au^- might appear in the PES(A) spectrum of Au_2^- at high photon fluxes. This possibility can be excluded for two reasons: (a) the PES(A) spectrum of Au^- does not exhibit a peak at 3.60 eV BE, and (b) the photon flux used in this experiment is relatively low (< 1 mJ/cm^2).

2. Electronically excited anions

In some cases (e.g., Al_2^- and Al_3^-) (Ref. 10), weak features observed in the PES(A) spectra were assigned to transitions from an excited state of the anion into the neutral states. Especially, a feature at lower BE than any feature corresponding to the PES(A) spectrum of the ground state anion appears. If peak B in the PES(A) spectrum of Au_2^- [Fig. 1(b)] is assigned to photoemission from electronically excited dimer anions in the beam, a peak at lower BE than peak A is expected to appear due to the transition from the anion excited state into the neutral ground state. This feature has not been observed. However, it might exhibit a very low relative intensity due to cross section effects.

3. Impurities

The mass resolution might not be sufficient to separate impurities such as oxides completely from the mass of the bare cluster. The resulting PES(A) spectrum is a sum of the spectrum of the bare cluster and the spectrum of the impurity (e.g., Au_2O^-). However, we did not observe any impurities in the mass spectra of Au cluster anions.

At present, an unambiguous assignment of feature B in the PES(A) spectrum of Au_2^- is not possible.

B. Au_3^-

The neutral trimers of the alkali [e.g., Na (Refs. 13 and 40)] and group I b (Cu,Ag,Au) (Refs. 2, 12, 17, 20, and 24–26) clusters are triangular. The negatively charged trimers are linear[2,40–43] with a $^1\Sigma_g^+$ ground state. The PES(A) spectra[8,10,40–42,44] of most of these species (Na_3^-, K_3^-, Rb_3^-, Cu_3^-, and Ag_3^-) exhibit a certain pattern: They display two dominant features corresponding to the transition into the neutral ground state $^2\Sigma_u^+$ and the first excited state $^2\Sigma_g^+$ of the linear isomer[2,44] of the neutral trimer. The PES(A) spectra of Cu_3^- (Refs. 1–4, 35, and 44) and Au_3^- [Fig. 1(c)] differ from the ones of Ag_3^- (Refs. 2, 4, and 44) and the alkali trimer anions[8] by the hybridization between the s and d orbitals. Due to a mixing of $4s$- and $3d$-derived orbitals, the peak corresponding to the $^2\Sigma_u^+$ state of Cu_3 exhibits a splitting into three components.[35,44] In the PES(A) spectrum of Au_3^- [Fig. 1(c)], more than two features (B–H) are found at BEs close to the VDE (peak A) and therefore this spectrum differs reasonably from the spectra of the other trimers. Au_3^- is predicted[20,26] to be linear with a $^1\Sigma_g^+$ ground state similar to the other discussed monovalent metal trimers anions. This structural prediction is confirmed by a recent high resolution PES(A) study.[31]

One reason for the different behavior of Au is the higher BE of the $6s$-derived orbitals. In the case of Au_3^-, the two transitions ($^2\Sigma_u^+ \leftarrow ^1\Sigma_g^+$ and $^2\Sigma_g^+ \leftarrow ^1\Sigma_g^+$) corresponding to photoemission from the two occupied $6s$-derived orbitals are located at BEs very close or within the manifold of states corresponding to photoemission from $5d$-derived orbitals. If a particle exhibits several close lying electronic states, the configuration interaction might disturb the symmetry of these states. Then a single state can correspond to a linear combination of several configurations. According to calculations,[20,26] the neutral linear trimer has a $^2\Sigma_u^+$ ground

state. The calculated BE[26] of the ground state transition (VDE) is 3.8 eV, in reasonable agreement with the position of peak A (3.89 eV) and also in agreement with earlier experimental data.[2,4] The ground state exhibits nearly no contributions from configurations of other electronic states.

The $^2\Sigma_g^+$ excited state of Au_3 lies within a manifold of other excited states of the trimer corresponding to the excitation of $5d$ electrons. Due to the possible configuration interaction, several excited states of the neutral might exhibit contributions from the $^2\Sigma_g^+$ state. In this case, no single peak in the PES(A) spectrum can be assigned to the $^2\Sigma_g^+$ state. However, as long as there is an excited state with a leading configuration of $^2\Sigma_g^+$ symmetry, a classification into $6s$- and $5d$-derived states is useful. For example the $^3\Sigma_u^+$ excited state of Au_2 lies very close ($\sim$0.2 eV) to the manifold of $^2S/^2D_{5/2}$-derived states, but has only a small contribution from these states (8%).[11,22]

It is possible to estimate the BE of the peak corresponding to the transition into the $^2\Sigma_g^+$ state. The difference in BE between the transition into the $^2\Sigma_g^+$ state and into the $^2\Sigma_u^+$ state for Ag_3^- is $\approx$1.2 eV as extracted from the PES(A) spectrum.[35,42] In Au clusters, the s orbitals are compressed due to relativistic effects and the bond lengths are shorter. Consequently, the $6s$ "bandwidth" is larger. For example, the energy spacing of the transitions into the $^1\Sigma_g^+$ state and the $^3\Sigma_u^+$ state of Au_2^- is about 1.25 times larger than the corresponding energy separation[2,35] for Ag_2^-. From these considerations, the BE of the $^2\Sigma_g^+$ state of Au_3^- is estimated to be about 5.4 eV. The difference in BE between the $^2\Sigma_u^+$ state and the $^2\Sigma_g^+$ state of Ag_3^- is multiplied by 1.25 and added to the BE of peak A of Au_3^-. The intensity of the feature should be about equal to the ground state peak in the PES(A) spectrum according to the comparison to the PES(A) spectra of the other monovalent metal trimers.[8,10,40–42,44] This makes peak F a good candidate for the transition into the $^2\Sigma_g^+$ state.

This very crude estimate is supported by calculations.[24] Calculations including the d-electron interaction predict a $^2\Sigma_g^+$ energy of the linear Ag_3 of 0.96 eV with respect to the neutral ground state. The same calculation yields an energy difference between the two Σ states of 1.08 eV for Au_3. The result on Ag_3 is too small by a factor of 1.25 compared to the experimental result.[4,35] If the calculated value of Au_3 is scaled by the same factor, an excitation energy of 1.35 eV ($=5.24$ eV BE) results. This is in reasonable agreement with the above estimates.

Analogous to the case of the dimer, the excitation energies of the neutral excited states as extracted from the PES(A) spectrum (Fig. 1) are listed in Table III. Only one excited state (presumably $^4E'$) has been found in R2PI experiments. This quartet $\leftarrow$ doublet transition cannot be observed in PES(A) due to the selection rules.

According to the tentative assignments (s.a.), the features B–E, G, and H correspond to transitions into d-derived excited states. Analogous to the considerations presented for Au_2^-, the neglect of shake-up processes yields the assignment of the observed features to excitations of a single $5d$ electron into one $6s$-derived orbital.

The manifold of d-derived states might be still separated

TABLE III. Excitation energies of the excited states of Au_3 as extracted from the PES(A) spectra. The excitation energy is calculated as in Table II (VDE=3.89 eV). Notations in parentheses are either uncertain (question mark) or refer to the linear neutral isomer (see the text). All values are given in electron volts. The uncertainty of the differences of the measured BEs is $\pm$15 meV.

Peak	Experimental excitation energy	Notation
A	0.00	$X\ ^2E'(^2\Sigma_u^+)$
B	0.49	
C	0.73	
D	0.84	
E	1.39	
F	1.47	$(^2\Sigma_g^+?)$
G	1.64	
H	2.01	

into $d_{5/2}$- and $d_{3/2}$-derived states. In a low resolution PES(A) spectrum[4] taken at $h\nu=7.9$ eV, a gap of about 0.3 eV located at 6.1 eV BE is found. However, the size of this gap is comparable to the average distance between neighboring peaks, and therefore the assignment to a "band gap" between $d_{5/2}$- and $d_{3/2}$-derived states is rather uncertain. The density of states in bulk Au (Ref. 16) exhibits two maxima corresponding to the $d_{5/2}$- and $d_{3/2}$-derived bands split by about 1.3 eV. There is a minimum in the density of states between the two maxima, but there is no distinct band gap. Therefore, the gap is expected to vanish with increasing cluster size.

C. Au_4^-

Table IV lists the excitation energies of the states of Au_4^- analogous to Tables II and III. To our knowledge, no R2PI spectra of the tetramer are published. Recent calculations[27] predict the existence of several low lying electronic excited states of Au_4 with different geometries. The excitation energy with respect to the neutral ground state depends strongly on the geometry of the cluster. Therefore, for comparison with the PES(A) spectrum, calculations on the excited states of the neutral tetramer assuming a geometric structure equal to the anion ground state are necessary. However, the compari-

TABLE IV. Excitation energies of the excited states of Au_4 as extracted from the PES(A) spectra up to 2.5 eV. The excitation energy is calculated as in Table II (VDE=2.78 eV). Dominant features are marked by bold characters. The notations refer to the corresponding electronic states (Ref. 42) of Ag_4. All values are given in electron volts. The uncertainty of the differences of the measured BEs is $\pm$15 meV.

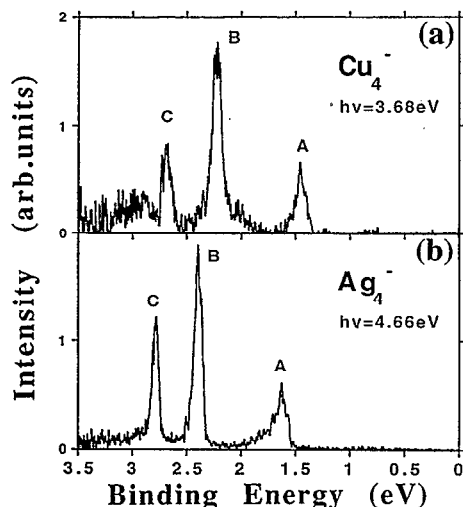| Peak	Experimental excitation energy	Notation[a]
A	**0.00**	(^1A_g)
B	0.64	
C	**1.54**	
D	**1.66**	$(^3B_{1g})$
E	2.01	
F	**2.17**	
G	**2.32**	$(^1B_{1g})$
H	2.48	

[a]Reference 42.

FIG. 2. A comparison of PES(A) spectra of Cu_4^- taken at $h\nu = 3.68$ eV photon energy (N_2 laser) and Ag_4^- taken at $h\nu = 4.66$ eV photon energy (Yag-laser, 4.Harmonic), respectively. The assignments of peaks A, B, and C are discussed in the text.

son with similar PES(A) spectra of the Cu_4^- and Ag_4^- [Figs. 2(a) and 2(b)] clusters yields some qualitative interpretation of the features displayed in Fig. 1.

As already discussed, the $6s$-derived molecular orbitals of the Au clusters are contracted by relativistic effects. Therefore, the corresponding BEs of these orbitals are higher, the bond lengths shorter, and the $6s$ "bandwidth," i.e., the difference in BE of the bonding and antibonding orbitals, is larger. For the dimer and trimer, we found an about 1.2 times larger spacing between the $6s$-derived states with respect to the corresponding $5s$-derived states in Ag clusters (s.a.).

Figures 2(a) and 2(b) display the spectra of Cu_4^- and Ag_4^- taken at $h\nu = 3.68$ and 4.66 eV photon energies, respectively. The two PES(A) spectra are strikingly similar in the BE range up to 3.5 eV. Because of this similarity, the corresponding states are presumably s derived. Three features dominate the PES(A) spectra of Ag_4^- and Cu_4^-: a small peak (A) at lowest BE (1.65 eV BE for Ag_4^-); an about two times larger peak (B) at 1.5 eV higher BE (2.39 eV BE for Ag_4^-), and a peak (C) with an intensity similar to the first feature close to the large peak (2.76 eV BE for Ag_4^-). For Ag_4^-, these features can be assigned[42] to transitions from the anion ground state ($^2B_{2u}$, rhombic geometry) to the neutral ground state (^1A_g) and two low lying excited states ($^3B_{1g}$ and $^1B_{1g}$).

There are three peaks with a relatively high intensity (area) for Au_4^-, two of them split into double peaks: feature A, features C/D, and features G/F. By analogy to the spectrum of Ag_4^-, we would argue that these structures in the Au_4^- spectrum have the corresponding origin as the structures A, B, and C in the Ag_4^- spectrum. At the relatively low photon energy used in our experiment, the photoemission cross section for electrons occupying an s-like orbital is larger than for electrons occupying a d orbital. This explains the enhanced intensity of the s-derived features. The cross section effect also explains the relatively low intensity of

features B and C with respect to the intensity of peak A in the spectrum of Au_4^- [Fig. 1(a)]. Features B and C correspond to photoemission from the $5d_{5/2}$ and $5d_{3/2}$ atomic orbitals occupied by six and four electrons, respectively, and should therefore exhibit a two to three times higher intensity than peak A. Peak A corresponds to photoemission from the $6s$ orbital occupied by two electrons.

A pattern similar to the pattern of the $4s$- and $5s$-derived low lying excited states of the Cu and Ag tetramers can be identified if the energy scale is altered by two modifications: (i) a shift to higher BE corresponding to a change in the VDE; and (ii) an enlargement of the spacings between the peaks. The enlargement of the spacings corresponds to shorter bond lengths and a larger $6s$ bandwidth. For the Au dimer and trimer, the scaling factor is only 1.2 for the comparison with Ag_2^- and Ag_3^-, whereas for Au_4^-, the scaling factor is about 2.

The relative large scaling factor for the tetramer might correspond to a higher binding energy per atom, i.e., stability, of the Au tetramer anion compared to Ag_4^-. According to the tight binding approximation, the bandwidth depends exponentially on the bond length between next neighbors and is correlated with the bond strength. Therefore, the scaling factor between $5s$- and $6s$-derived manifolds of states in Ag and Au clusters might change with the cluster size depending on various structural parameters like the geometry and the degree of the $s-d$ hybridization. Especially, a strong $s-d$ hybridization might result in an enhancement of the bond strength. The splitting of the features marked B/C and G/F into double peaks supports the picture of a strong $s-d$ mixing. A similar splitting is observed in the PES(A) spectrum[35,44] of Cu_3^-.

The observation of a similar pattern of the s-derived electronic states for Au and Ag corresponds to a similarity of the geometric structure. Therefore, we tentatively assign the features A, $D+C$, and $G+F$ to transitions from a rhombic anion electronic ground state $^2B_{2u}$ into the ground state of the neutral ^1A_g and two excited states $^3B_{1g}$ and $^1B_{1g}$, respectively. The manifold of states observed at BEs beyond peak G (features $H-O$) corresponds presumably to excitations of $5d$ electrons. An assignment of this multitude of states seems very difficult, even if high level calculations and vibrational resolved data would be available.

Feature A [Au_4^- (Fig. 1)] is assigned to the transition into the neutral ground state. The weak feature A' has not been found in earlier experiments[2,4] and might result from electronically excited Au_4^- present in the beam. The same consideration applies to feature B.

D. A comparison of Au_2^-, Au_3^-, and Au_4^-

The three clusters exhibit a strong even–odd alternation of the VDE. This has been also observed for Cu and Ag clusters[1–4,35,42,44] and corresponds to the alkali-like behavior of the coinage metals. The large amplitude of the alternation (≈ 2 eV for Au_2^-/Au_3^-) can be explained by the relativistic contraction of the $6s$ orbitals. This also shows that the highest energy feature corresponds to the removal of an extra s electron.

The $5d$-derived manifold of states does not exhibit an even–odd alternation. The upper edge of the $5d$ "band" seems to shift gradually from ≈ 4.2 eV (Au_2^-) to ≈ 4.8 eV (Au_4^-). This is a consequence of the fact that the energy reference level is the vacuum level (and not the BE of the HOMO). Similar behavior is found in the PES(A) spectra of Cu_n^- clusters.[3,35,44] The gradual increase of the BE of the d "band" is caused by the enlarged number of neighbors due to the not completely screened attractive potentials of the neighboring atoms.

The number of peaks in the spectra seems to exhibit an even–odd alternation, too. For particles with LS coupling dominated by singlet or doublet states of the anions[42] (such as the alkali cluster anions[40,41]), this is to be expected. According to the photodetachment selection rules, a transition from a singlet initial state can only occur into a doublet state of the neutral, while doublet anion states allow for transitions into singlet and triplet states. According to this simple model, PES(A) spectra of anions with an odd number of electrons exhibit twice the number of peaks. For electrons with a strong spin–orbit coupling, the spin degeneracy is removed and the simple picture is no longer valid.

For Au_4^-, the number of peaks is already that high, that even at the high resolution available in our experiment, the features start to overlap. The effort to assign the d-derived emission features to individual electronic configurations seems very difficult even for small clusters with $n < 5$.

VI. CONCLUSIONS

PES(A) spectra of small Au_n^- clusters with $n = 2-4$ were compared to results of R2PI spectroscopy.[11,12] In the case of the dimer, all five excited states found in R2PI experiments on the neutral can be assigned to features in the PES(A) spectrum. Only minor shifts of the extracted excitation energies are found due to the differences of the Franck–Condon profiles. It has been demonstrated that PES(A) spectra can serve as a map of the electronic states of a cluster, while the high resolution of the R2PI method gains information about the symmetry of the states. However, with increasing cluster size, less or no excited states of a particle have been detected using R2PI.

A certain correspondence is observed with the spectra of Cu_n^- and Ag_n^- clusters if the relativistic contraction of the Au $6s$ orbitals and the large spin–orbit splitting of the $5d$ orbitals are taken into consideration. The mixing between the $6s$ and $5d$ orbitals in Au is larger than between the corresponding orbitals in Cu and Ag clusters. In the case of the tetramers, the similarity of the s-derived features is striking if the data are corrected for the higher BE of the $6s$ states and the larger splitting of bonding–antibonding states. Therefore, we conclude that despite the differences in the PES(A) spectra, the small Au clusters exhibit a certain structural similarity to Cu and Ag clusters.

ACKNOWLEDGMENTS

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