



Probing the electronic and vibrational structure of Au2Al2 – and Au2Al2 using photoelectron spectroscopy and high resolution photoelectron imaging

Gary V. Lopez, Joseph Czekner, Tian Jian, Wei-Li Li, Zheng Yang, and Lai-Sheng Wang

Citation: The Journal of Chemical Physics **141**, 224309 (2014); doi: 10.1063/1.4903784 View online: http://dx.doi.org/10.1063/1.4903784 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/22?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Probing the electronic structure and Au–C chemical bonding in AuC2 – and AuC2 using high-resolution photoelectron spectroscopy J. Chem. Phys. **140**, 084303 (2014); 10.1063/1.4865978

Resonant photoelectron spectroscopy of Au2 – via a Feshbach state using high-resolution photoelectron imaging J. Chem. Phys. **139**, 194306 (2013); 10.1063/1.4830408

Communication: Vibrational spectroscopy of Au4 from high resolution photoelectron imaging J. Chem. Phys. **139**, 021106 (2013); 10.1063/1.4813503

High resolution photoelectron imaging of Au2 – J. Chem. Phys. **138**, 184304 (2013); 10.1063/1.4803477

Ground state structures and photoelectron spectroscopy of [Co m (coronene)] – complexes J. Chem. Phys. **126**, 084306 (2007); 10.1063/1.2437202



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 128.148.231.12 On: Sun, 08 Feb 2015 16:14:17



Probing the electronic and vibrational structure of $Au_2Al_2^$ and Au_2Al_2 using photoelectron spectroscopy and high resolution photoelectron imaging

Gary V. Lopez, Joseph Czekner, Tian Jian, Wei-Li Li, Zheng Yang, and Lai-Sheng Wang^a) Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

(Received 13 October 2014; accepted 25 November 2014; published online 11 December 2014)

The electronic and vibrational structures of $Au_2Al_2^-$ and Au_2Al_2 have been investigated using photoelectron spectroscopy (PES), high-resolution photoelectron imaging, and theoretical calculations. Photoelectron spectra taken at high photon energies with a magnetic-bottle apparatus reveal numerous detachment transitions and a large energy gap for the neutral Au_2Al_2 . Vibrationally resolved PE spectra are obtained using high-resolution photoelectron imaging for the ground state detachment transition of $Au_2Al_2^-$ at various photon energies (670.55–843.03 nm). An accurate electron affinity of 1.4438(8) eV is obtained for the Au_2Al_2 neutral cluster, as well as two vibrational frequencies at 57 ± 8 and 305 ± 13 cm⁻¹. Hot bands transitions yield two vibrational frequencies for $Au_2Al_2^-$ at 57 ± 10 and 144 ± 12 cm⁻¹. The obtained vibrational and electronic structure information is compared with density functional calculations, unequivocally confirming that both $Au_2Al_2^-$ and Au_2Al_2 possess C_{2v} tetrahedral structures. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4903784]

I. INTRODUCTION

Doped gold clusters provide opportunities to tune the properties as a function of composition and may lead to the design of novel materials.¹⁻⁶ Hence, they have attracted increasing attention in recent years.⁶⁻¹⁰ Photoelectron spectroscopy (PES) has been combined with theoretical calculations as an effective approach to study the electronic and structural properties of bimetallic gold-containing clusters.^{2,11–26} Specifically, the prediction of highly stable MAu_{12} (M = W and Mo) clusters with a large energy gap⁸ was quickly confirmed by PES experiments.⁷ The enhanced stability of the metal-doped Au₁₂ cluster was attributed to aurophilic attractions, relativistic effects, and a closed-shell electron configuration.²⁷ The enhanced stability for specific bimetallic gold clusters has been investigated using the electronic shell-model.¹⁰ Halogen-like behavior of Au atoms was proposed in transition-metal doped MAu₄ clusters, which were found to prefer tetrahedral structures.²⁸ Hydrogen-like behavior of Au atoms was found in a series of boron-gold and silicon-gold bimetallic clusters,^{26,29-31} which were confirmed by PES and theoretical studies. However, transitionmetal doped Au_6M (M = Ti, Cr, and V) clusters were found to possess planar structures with the central M atom exhibiting atom-like magnetism.⁹ Clearly, the structures of doped Au clusters depend on the nature of bonding between the dopant atom and the gold clusters. Although most of the studies have focused on the interaction of Au clusters with transition-metal dopants,^{1,7,9,10,20,24,28,32-34} relatively few studies are available concerning the interactions of main group elements with Au clusters.^{35–40}

Due to the limited resolution in conventional PES studies (10–40 meV), PE imaging has become a powerful alterna-

tive PES approach after the implementation of the velocitymap imaging (VMI) technique for the past decade.⁴¹ VMI allows very low kinetic energy electrons to be detected and provides a much higher resolution method for PES.⁴² Recently, the Wang group has developed a high resolution photoelectron imaging system to study size-selected cluster anions produced from a laser vaporization supersonic cluster source,⁴³ where vibrationally resolved photoelectron images for the ground state detachment transitions of Au₂⁻ and of a Y-shaped Au₄⁻ were obtained^{44–46} while autodetachment processes in the high-resolution photoelectron spectra of Au₂⁻⁴⁷ and the electronic structure and Au–C chemical bonding in AuC₂⁻ and AuC₂ were also studied.⁴⁸

In the current article, we report a combined study on $Au_2Al_2^-$ an Au_2Al_2 using conventional PES, high-resolution PE imaging, and theoretical calculations. An accurate electron affinity of 1.4438(8) eV, as well as two vibrational frequencies (57 and 305 cm⁻¹), are obtained for the Au_2Al_2 neutral cluster from the high resolution PE imaging, whereas the conventional PES at high photon energies reveal a large energy gap. Vibrational hot bands also yield two vibrational frequencies for the $Au_2Al_2^-$ anionic cluster (57 and 144 cm⁻¹). Global minimum searches lead to a C_{2v} tetrahedral structure for the anionic and neutral Au_2Al_2 , which are confirmed by both the calculated frequencies and the simulated PE spectrum.

II. EXPERIMENTAL METHODS

A. Magnetic-bottle photoelectron spectroscopy

The $Au_2Al_2^{-}$ cluster was first studied using a magneticbottle PES apparatus equipped with a laser vaporization supersonic cluster source, details of which can be found in Ref. 49. Briefly, cluster anions were produced by focusing a pulsed laser beam onto a disk target made of Al and Au (1:4

^{a)}E-mail: Lai-Sheng_Wang@brown.edu

ratio by mass) in the presence of a helium carrier gas seeded with 5% Ar. The laser-induced plasma was cooled by the carrier gas initiating nucleation and cluster formation. Clusters were entrained in the carrier gas and underwent a supersonic expansion. Negatively charged clusters were extracted from the cluster beam and analyzed by a time-of-flight (TOF) mass spectrometer. The Au₂Al₂⁻ cluster of current interest was mass-selected and decelerated before being photodetached by a laser beam. Three detachment photon energies from either a Nd:YAG laser (355 and 266 nm) or an ArF excimer laser (193 nm) were used in this study. Photoelectrons were collected at nearly 100% efficiency and analyzed in a 3.5 m long electron flight tube. The PE spectra were calibrated by using the known spectra of Au⁻ and Bi⁻. The resolution of the apparatus, $\Delta E_k/E_k$, was better than 2.5%, i.e., ~25 meV for 1 eV electron.

B. High resolution PE imaging

The high-resolution PE imaging apparatus, consisting of a laser vaporization supersonic cluster source, a time-of-flight mass spectrometer, and a new VMI lens system, has been recently described.⁴³ The cluster source is similar to that on our magnetic-bottle PES apparatus. Clusters formed inside the nozzle were entrained by a helium carrier gas seeded with 10% Ar carrier gas and underwent a supersonic expansion. The Au₂Al₂⁻ cluster was mass-selected and focused into the interaction zone of the collinear VMI system, where they were detached by a laser beam. Photoelectrons were accelerated toward a position-sensitive detector with a 75 mm diameter micro-channel plate coupled to a phosphor screen and a charge-coupled device (CCD) camera. The tunable detachment radiation (670.55–843.03 nm, linewidth $< 0.3 \text{ cm}^{-1}$) used was from a Continuum Sunlite OPO system pumped by an injection-seeded Continuum Powerlite laser. A half-wave plate combined with a high-quality Glan-Laser polarizer was used to achieve a high degree of polarization parallel to the imaging detector plane. Photoelectron images were averaged with 50 000 to 200 000 laser shots. Inverse-Abel transformation was used to obtain the three-dimensional (3D) electron distributions from the recorded two-dimensional (2D) images. Calibration of the imaging system was done using the known spectrum of Au⁻. The reconstruction was done in both the BASEX⁵⁰ and pBASEX⁵¹ programs.

III. THEORETICAL METHODS

The search for the global minimum structure of $Au_2Al_2^{-}$ was performed using the simulated annealing algorithm^{52–55} coupled with DFT geometry optimization, where the generalized gradient approximation was used with the Perdew-Burke-Ernzerhof (PBE) functional⁵⁶ and the Los Alamos ECP plus DZ (LANL2DZ)⁵⁷ basis set. The low-lying isomers of $Au_2Al_2^{-}$ were re-optimized using the PBE0 and the PW91⁵⁸ functionals with the Stuttgart'97⁵⁹ basis set for Au and the aug-cc-pCVTZ⁶⁰ basis set for Al. The optimized geometry of the anion was used as the initial geometry in the optimization and single point energy calculation of the neutral cluster.

Harmonic vibrational frequencies were computed to ensure that the low energy isomers are true minima and to compare with the experimental results. The first vertical detachment energy from the optimized Au₂Al₂⁻ was calculated as the energy difference between the neutral and anion at the anion structure. The excitation energies of the deeper orbitals were calculated using time-dependent-DFT (TD-DFT)⁶¹ and added to the first VDE to approximate the VDEs of the excited states. Each VDE was fitted with a Gaussian of 0.1 eV width to yield a simulated PE spectrum while the relative intensities used for the VDEs were assigned empirically on the basis of the spin multiplicities of the final states, one for singlet and two for triplet final states. This approach has been used extensively in elucidating the structures of size-selected clusters previously.⁶² All these calculations were done using NWChem.63

IV. EXPERIMENTAL RESULTS

A. High photon energy spectra using the magnetic-bottle apparatus

Fig. 1 displays the spectra of $Au_2Al_2^-$ at three photon energies obtained with the magnetic-bottle PES apparatus. In each spectrum, the X band represents the transition from the anionic ground state to that of the neutral. The A, B, ... bands denote transitions to the excited states of the neutral species. The weak signal labeled as *a* represents a transition that will be explained later. All the VDEs are summarized in Table I, where they are compared with theoretical results.

The 355 nm spectrum (Fig. 1(a)) displays a sharp feature X at a VDE of 1.48 ± 0.05 eV. This sharp peak suggests a minimal geometry change upon photodetachment. The adiabatic detachment energy (ADE) of this band, which also



FIG. 1. Photoelectron spectra of $Au_2Al_2^-$ at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), and (c) 193 nm (6.424 eV) obtained from the magnetic-bottle PES apparatus.

| | VDE (eV) ^a (Expt.) | Final state and electronic configuration | VDE (eV) ^b (Theor.) |
|---|-------------------------------|---|--------------------------------|
| X | 1.4438(8) ^c | ${}^{1}A_{1} \dots 2b_{2}{}^{2}2b_{1}{}^{2}4a_{1}{}^{2}3b_{1}{}^{2}2a_{2}{}^{2}3b_{2}{}^{2}4b_{1}{}^{2}5a_{1}{}^{2}6a_{1}{}^{0}$ | 1.53 |
| А | 3.21(4) | ${}^{3}A_{1} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{2}4b_{1}^{2}5a_{1}^{1}6a_{1}^{1}$ | 2.81 |
| В | 3.70(4) | ${}^{3}B_{2}\dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{1}4b_{1}^{2}5a_{1}^{2}6a_{1}^{1}$ | 3.41 |
| С | 3.81(4) | ${}^{1}A_{1}^{2}\dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{2}4b_{1}^{2}5a_{1}^{1}6a_{1}^{1}$ | 3.70 |
| | | ${}^{1}B_{1} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{2}4b_{1}^{1}5a_{1}^{2}6a_{1}^{1}$ | 3.72 |
| D | 3.95(4) | ${}^{3}B_{1} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{2}4b_{1}^{1}5a_{1}^{2}6a_{1}^{1}$ | 3.98 |
| Е | 4.66(8) | ${}^{1}B_{2} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{2}3b_{2}^{1}4b_{1}^{2}5a_{1}^{2}6a_{1}^{1}$ | 4.71 |
| | | ${}^{3}B_{1} \dots 2b_{2} {}^{2}2b_{1} {}^{2}4a_{1} {}^{2}3b_{1} {}^{1}2a_{2} {}^{2}3b_{2} {}^{2}4b_{1} {}^{2}5a_{1} {}^{2}6a_{1} {}^{1}$ | 6.18 |
| | | ${}^{3}A_{2} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{1}3b_{2}^{2}4b_{1}^{2}5a_{1}^{2}6a_{1}^{1}$ | 6.18 |
| | | ${}^{3}A_{1} \dots 2b_{2} {}^{2}2b_{1} {}^{2}4a_{1} {}^{1}3b_{1} {}^{2}2a_{2} {}^{2}3b_{2} {}^{2}4b_{1} {}^{2}5a_{1} {}^{2}6a_{1} {}^{1}$ | 6.24 |
| | | ${}^{1}A_{2} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{2}3b_{1}^{2}2a_{2}^{1}3b_{2}^{2}4b_{1}^{2}5a_{1}^{2}6a_{1}^{1}$ | 6.25 |
| | | ${}^{1}B_{1} \dots 2b_{2} {}^{2}2b_{1} {}^{2}4a_{1} {}^{2}3b_{1} {}^{1}2a_{2} {}^{2}3b_{2} {}^{2}4b_{1} {}^{2}5a_{1} {}^{2}6a_{1} {}^{1}$ | 6.33 |
| | | ${}^{3}B_{1} \dots 2b_{2} {}^{2}2b_{1} {}^{1}4a_{1} {}^{2}3b_{1} {}^{2}2a_{2} {}^{2}3b_{2} {}^{2}4b_{1} {}^{2}5a_{1} {}^{2}6a_{1} {}^{1}$ | 6.38 |
| | | $^{1}A_{1} \dots 2b_{2}^{2}2b_{1}^{2}4a_{1}^{1}3b_{1}^{2}2a_{2}^{2}3b_{2}^{2}4b_{1}^{2}5a_{1}^{2}6a_{1}^{1}$ | 6.46 |

TABLE I. The observed vertical detachment energies (VDEs) for Au2Al2-, compared with theoretical calculations.

^aNumbers in the parentheses represent experimental uncertainties in the last digit

^bCalculated at PW91/Al/Aug-cc-pCVTZ/Au/Stuttgart'97 level of theory.

^cThe experimental value from our magnetic bottle TOF PE spectrometer is 1.48(5) eV.

represents the electron affinity (EA) of Au₂Al₂, is estimated by drawing a straight line along the rising edge of band X and then adding the instrumental resolution to its intersection with the binding energy axis. The ADE value was evaluated to be 1.40 ± 0.05 eV. Following a large energy gap (~1.7 eV) and a weak band a, a broad and intense band A is observed with a VDE of 3.21 ± 0.04 . The large energy gap between bands X and A suggests that neutral Au₂Al₂ is closed shell with a large gap between its highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. The spectrum at 266 nm (Fig. 1(b)) reveals three closely-lying detachment features: B (VDE: 3.70 eV), C (VDE: 3.81 eV), and D (VDE: 3.95 eV). At 193 nm (Fig. 1(c)), no distinct detachments are observed except some weak continuous signals (E) in the high binding energy side. One weak feature labeled as a at 2.40 eV is observed in all three spectra in Fig. 1. It is most likely due to autodetachment, as observed in a number of other clusters with large HOMO-LUMO gaps.^{64–66} It could also be due to a hydride contamination, as observed in the case of $Au_2^{-.67}$

B. High resolution PE imaging

We also obtained high-resolution PE spectra of the ground state transition (X) using PE imaging at four photon energies, as shown in Fig. 2. The spectrum taken at 670.55 nm (Fig. 2(d)) resolves a short vibrational progression with a frequency of $305 \pm 13 \text{ cm}^{-1}$. At 775.10 nm (Fig. 2(c)), a low frequency progression is clearly resolved off the peak corresponding to the 0-0 transition with a frequency of 57 \pm 8 cm⁻¹. The low frequency mode is resolved even better at 826.12 nm (Fig. 2(b)) and 843.03 nm (Fig. 2(a)). In addition, the low photon energy spectra (Fig. 2(a) and b) resolve two weak features at the low binding energy side, labeled as '*'. These features are due to vibrational hot bands of $Au_2Al_2^{-}$, yielding two anion vibrational frequencies at 57 \pm 10 and $144 \pm 12 \text{ cm}^{-1}$. More importantly, the 843.03 nm spectrum (Fig. 2(a)) yields the most accurate measurement of the EA



FIG. 2. Photoelectron spectra of Au₂Al₂- obtained from the PE imaging at (a) 843.03 nm (1.4707 eV), (b) 826.12 nm (1.5008 eV), (c) 775.10 nm (1.5996 eV), and (d) 670.55 nm (1.8490 eV). The vertical lines represent vibrational structures. Vibrational hot bands are labeled with *.

for the Au_2Al_2 cluster as 1.4438 ± 0.0008 eV, which is significantly more accurate than that afforded by the magnetic-bottle apparatus (Fig. 1).

V. THEORETICAL RESULTS

Fig. 3 shows the optimized structures of the three lowestlying isomers of $Au_2Al_2^-$ and the global minimum of Au_2Al_2 , obtained at the PW91/Al/Aug-cc-pCVTZ/Au/Stuttgart'97 level of theory. The global minimum of $Au_2Al_2^-$ (²A₁) is a tetrahedral structure with C_{2v} symmetry (Fig. 3(a)). Neutral Au_2Al_2 (¹A₁, shown in Fig. 3(b)) has an almost identical structure as the anion with little structural change: Al-Al and Al-Au distances are slightly decreased by 0.03–0.05 Å in the neutral, whereas the Au-Au distance is increased by 0.02 Å in the neutral. The current results are in good agreement with a previous calculation.⁶

The relative energies calculated at the PW91 level of theory (Fig. 3(a)) show that the global minimum of $Au_2Al_2^{-1}$ is significantly more stable than the nearest low-lying isomer (9 Kcal/mol higher). Thus, the contributions of other isomers to the experiment can be ruled out. The ADE and VDEs of the global minima were calculated for comparison with the experimental data. The calculated ADE and the first VDE at two levels of theory and basis sets are given in Table II, Both PBE0 and PW91 give consistent results, within 0.07 to 0.09 eV of the experimental values.

To help assign the observed vibrational modes, we calculated the frequencies for the C_{2v} structures of both anionic and neutral clusters, as given in Table III. The displacement vectors of the normal modes of Au_2Al_2 are shown in Fig. 4 while a description of the normal modes and symmetries for



FIG. 3. Optimized structures and symmetries for (a) $Au_2Al_2^{-}$ and (b) Au_2Al_2 , at PW91/Al/Aug-cc-pCVTZ/Au/Stuttgart'97 level of theory. $\angle Au$ -Al-Au = 75.56°, $\angle Al$ -Al-Au = 57.84°, and $\angle Al$ -Au-Au = 52.22° for the C_{2v} anion and $\angle Au$ -Al-Au = 77.79°, $\angle Al$ -Al-Au = 57.61°, and $\angle Al$ -Au-Au = 51.11° for the neutral. Bond lengths are given in Å. The two low-lying isomer of $Au_2Al_2^{-}$ are also included.

TABLE II. Observed and calculated adiabatic detachment energy (ADE) and first VDE of $Au_2Al_2^-$ at different levels of theory and basis sets. Al/Augcc-pCVTZ/Au/Stuttgart'97 level of theory was used in all the cases and all energies are in eV.

| | | ADE | VDE |
|-------------------------|------|-----------|-----------|
| Theory | PBE0 | 1.49 | 1.52 |
| | PW91 | 1.51 | 1.53 |
| Experiment ^a | | 1.4438(8) | 1.4438(8) |

^aNumbers in the parentheses present experimental uncertainties in the last digit.

both $Au_2Al_2^-$ and Au_2Al_2 are given in Table III, with three totally symmetric modes (a_1) in each case. The results for the anion and neutral are very similar, because of the small geometry change. Table III compares the calculated frequencies with the experimental results.

VI. DISCUSSION AND COMPARISON BETWEEN EXPERIMENT AND THEORY

The molecular orbitals of Au_2Al_2 are shown in Fig. 5, where the extra electron in the anion resides in the 6a1 LUMO (i.e., SOMO in the anion). The first detachment channel corresponds to the removal of the electron from the $6a_1$ SOMO. The calculated first VDE (Table II) of 1.53 eV at PW91 or 1.52 eV at PBE0 is in excellent agreement with the experimental values of 1.4438 eV. Two vibrational modes are observed with frequencies of 57 and 305 cm^{-1} , which are in excellent agreement with the calculated frequencies of the v_3 and v_1 totally symmetric modes, respectively (Table III and Fig. 4). As described in Table III and also shown in Fig. 4, the v_3 mode involves primarily symmetric Au–Au stretching and the Al atoms moving away from the Au-Au axis. The activation of this mode is in excellent agreement with the geometry change from the anion to the neutral of slightly shorter Au-Al bonds and a slightly longer Au-Au bond. The v_1 mode involves symmetric Al-Al stretching and the activation of the mode also agrees well with the slight Al-Al bond change between the anion and the neutral. Furthermore, the observed two frequencies for the anion (57 and 144 cm^{-1}) from the hot

TABLE III. Comparison between the experimental vibrational frequencies and theoretical calculations (unscaled) for the global minimum C_{2v} tetrahedral structure of Au_2Al_2 and $Au_2Al_2^{-}$.

| | Mode | Symmetry | Description | Calc. | Expt. ^a |
|--|----------------|-----------------------|-----------------------------|-------|--------------------|
| Au ₂ Al ₂ | v ₁ | <i>a</i> ₁ | Symmetric Al-Al stretching | 307 | 305(13) |
| 2 2 | v_2 | a_1 | Symmetric Al-Al bending | 157 | |
| | ν_3 | a_1 | Symmetric Au-Au stretching | 56 | 57(8) |
| | v_4 | a_2 | Al-Al rocking | 177 | |
| | v_5 | b_1 | Asymmetric Al-Al stretching | 238 | |
| | v ₆ | b_2 | Al-Al rocking | 216 | |
| Au ₂ Al ₂ ⁻ | v_1 | $\bar{a_1}$ | Symmetric Al-Al stretching | 309 | |
| 2 2 | v_2 | a_1 | Symmetric Al-Al bending | 154 | 144(12) |
| | ν_3 | a_1 | Symmetric Au-Au stretching | 52 | 57(10) |
| | v_4 | a_2 | Al-Al rocking | 152 | |
| | v_5 | b_1 | Asymmetric Al-Al stretching | 213 | |
| | v ₆ | b_2 | Al-Al rocking | 191 | |

^aNumbers in the parentheses present experimental uncertainties in the last digit.



FIG. 4. The normal modes and their symmetries of Au₂Al₂ at PW91/Al/Aug-cc-pCVTZ/Au/Stuttgart'97 level of theory. Displacement vectors are shown by blue arrows.

bands are also in good agreement with the calculated frequencies of the v_3 and v_2 modes for the anions (Table III).

The second electron detachment channel occurs from the $5a_1$ HOMO, leaving the final neutral species in the lowest triplet state $({}^{3}A_{1})$. The molecular orbital contour (Fig. 5) shows the HOMO has most electron density over the Al-Al and Au-Au atoms, in agreement with the Al-Al and Au-Au bond length change upon electron detachment. The calculated VDE of this detachment channel is 2.81 eV, compared to the VDE of band at 3.21 eV (Table I). The corresponding detachment into the singlet final state $({}^{1}A_{1})$ has a calculated VDE of 3.70 eV, which can contribute to band C at 3.81 eV. The next electron detachment occurs from the $3b_2$ (HOMO – 2), with a calculated VDE of 3.41 eV, in good agreement with band B at 3.70 eV. The calculated VDEs for higher detachment channels are all in reasonable agreement with the observed experimental features (Table I). The simulated spectrum at PW91/Al/Aug-cc-pCVTZ/Au/Stuttgart'97 is compared qualitatively with the 193 nm spectrum in Fig. 6.

The doped clusters can result in completely different structures relative to the bare clusters because both Au₄ and Al₄ are known to have 2D structures.^{45,68–73} Experimental and theoretical evidence of aromaticity in an all-metal system, the Al₄²⁻ dianion in a series of bimetallic and ionic clusters MAl₄- (M = Li, Na, or Cu) has been reported.⁶⁸ The Al₄²⁻ dianion, both as an isolated species and in the bimetallic molecules (MAl₄-, M = Li, Na, or Cu), was found to be square planar and to possess two delocalized π electrons conforming to the structural criterion and the (4n + 2) Hückel's rule for aromaticity.⁶⁸ The delocalization of the two π electrons is critical for the planar structure and aromaticity of



FIG. 5. Molecular orbitals and symmetries of Au_2Al_2 at PW91/Al/Aug-cc-pCVTZ/Au/ Stuttgart'97 level of theory.

 $Al_4^{2-.68}$ Thus, removing one or both of the π electrons breaks the delocalization hence modifying the square planar structure observed in Al_4^{2-} . The ground states of the Al_4 cluster and its anion have been predicted to have rhombuslike (D_{2h}) 2D symmetrical structures.⁶⁹ The tetramer of Au, on the other hand, is important as the neutral and anionic Au₄ clusters show different ground state geometries in the gas phase. Au₄⁻ has recently been confirmed to be a Y-shaped 2D (C_{2v}) structure by analyses of the vibrational resolved PE spectra obtained with our high resolution PE imaging apparatus,⁴⁵ while the neutral Au₄ was found to have a 2D rhombus (C_{2v}) structure. The planarity of gold clusters has been attributed to the strong relativistic effects of gold⁷⁰ which reduce its 5d-6s energy gap and enhance its s-d hybridization.^{71–73} The directional bonding and reduced Au-Au bond length as favored by the Au 5d electrons lead to the preference of planar geometries of the small gold clusters such as the tetramer of Au.⁷³ The 3D tetrahedral structures of the anion and neutral Au₂Al₂ species from this study are quite different from the anion and neutral Au₄ and Al₄ clusters. The doping of gold with Al atoms and vice versa dramatically affects the structure of the host anion and neutral Al₄ or Au₄ species. It seems that the Au-Al interactions are critical in determining the stability of the Au-Al alloy cluster. The 3D tetrahedral structures keep the Al-Al and Au-Au bonding while optimizing the Au-Al bonding.



FIG. 6. Comparison between the photoelectron spectrum at 193 nm and the simulated spectrum, which is obtained by fitting VDEs calculated at PW91/Al/Aug-cc-pCVTZ/Au/ Stuttgart'97 level of theory with unit area Gaussians of width 0.1 eV.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 128.148.231.12 On: Sun. 08 Feb 2015 16:14:17

VII. CONCLUSIONS

The current study demonstrates that conventional PES at high photon energies, high-resolution PE imaging, and density functional calculations complement each other to provide electronic, vibrational, and structural information for size-selected clusters. The high-resolution PE imaging spectra at lower photon energies are particularly powerful to reveal vibrational information, which rival infrared spectroscopy. The vibrationally resolved PE spectra unequivocally confirm the global minimum structure of the $Au_2Al_2^-$ and Au_2Al_2 bimetallic clusters to be 3D tetrahedral, which are quite different from the 2D structures of the anion and neutral Au_4 and Al_4 clusters.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-1263745). The calculations were done using the Center for Computation and Visualization (CCV) at Brown University.

- ¹H. Tanaka, S. Neukermans, E. Janssens, R. E. Silverans, and P. Lievens, J. Am. Chem. Soc. **125**, 2862 (2003).
- ²L. X. Zhao, T. T. Cao, X. J. Feng, L. Xiao, Y. M. Lei, and Y. H. Luo, J. Mol. Struct.: THEOCHEM **895**, 92 (2009).
- ³M. Zhang, L. M. He, L. X. Zhao, X. J. Feng, W. Cao, and Y. H. Luo, J. Mol. Struct.: THEOCHEM **911**, 65 (2009).
- ⁴L. Xiao, B. Tollberg, X. K. Hu, and L. C. Wang, J. Chem. Phys. **124**, 114309 (2006).
- ⁵X. B. Li, H. Y. Wang, X. D. Yang, Z. H. Zhu, and Y. J. Tang, J. Chem. Phys. **126**, 084505 (2007).
- ⁶Y. F. Li, Y. Li, and X. Y. Kuang, Eur. Phys. J. D 67, 132 (2013).
- ⁷X. Li, B. Kiran, J. Li, H. J. Zhai, and L. S. Wang, Angew. Chem., Int. Ed. **41**, 4786 (2002).
- ⁸P. Pyykkö and N. Runeberg, Angew. Chem., Int. Ed. **41**, 2174 (2002).
- ⁹X. Li, B. Kiran, L. F. Cui, and L. S. Wang, Phys. Rev. Lett. **95**, 253401 (2005).
- ¹⁰E. Janssens, H. Tanaka, S. Neukermans, R. E. Silverans, and P. Lievens, Phys. Rev. B 69, 085402 (2004).
- ¹¹W. Bouwen, F. Vanhoutte, F. Despa, S. Bouckaert, S. Neukermans, L. T. Kuhn, H. Weidele, P. Lievens, and R. E. Silverans, Chem. Phys. Lett. **314**, 227 (1999).
- ¹²M. B. Cortie, A. Maaroof, G. B. Smith, and P. Ngoepe, Curr. Appl. Phys. 6, 440 (2006).
- ¹³S. Neukermans, E. Janssens, H. Tanaka, R. E. Silverans, and P. Lievens, Phys. Rev. Lett. **90**, 033401 (2003).
- ¹⁴Q. Li, Y. Li, T. Cui, Y. Wang, L. J. Zhang, Y. Xie, Y. L. Niu, Y. M. Ma, and G. T. Zou, J. Phys.: Condens. Matter **19**, 425224 (2007).
- ¹⁵L. S. Hsu, Y. K. Wang, Y. L. Tai, and J. F. Lee, Phys. Rev. B 72, 115115 (2005).
- ¹⁶Y. Li, Y. P. Cao, Y. F. Li, S. P. Shi, and X. Y. Kuang, Eur. Phys. J. D 66, 10 (2012).
- ¹⁷D. Dong, Z. Ben-Xia, W. Hui, and D. Quan, Comput. Theor. Chem. **1025**, 67 (2013).
- ¹⁸D. Dong, K. Xiao-Yu, G. Jian-Jun, and Z. Ben-Xia, Physica A 389, 5216 (2010).
- ¹⁹M. Zhang, H. Y. Zhang, L. N. Zhao, Y. Li, and Y. H. Luo, J. Phys. Chem. A **116**, 1493 (2012).
- ²⁰K. Koyasu, Y. Naono, M. Akutsu, M. Mitsui, and A. Nakajima, Chem. Phys. Lett. **422**, 62 (2006).
- ²¹Q. Chen, H. Bai, H. J. Zhai, S. D. Li, and L. S. Wang, J. Chem. Phys. **139**, 044308 (2013).
- ²²Q. Chen, H. J. Zhai, S. D. Li, and L. S. Wang, J. Chem. Phys. **138**, 084306 (2013).
- ²³R. Pal, L. M. Wang, W. Huang, L. S. Wang, and X. C. Zeng, J. Chem. Phys. 134, 054306 (2011).
- ²⁴L. M. Wang, R. Pal, W. Huang, X. C. Zeng, and L. S. Wang, J. Chem. Phys. 132, 114306 (2010).

- ²⁵L. F. Cui, Y. C. Lin, D. Sundholm, and L. S. Wang, J. Phys. Chem. A 111, 7555 (2007).
- ²⁶X. Li, B. Kiran, and L. S. Wang, J. Phys. Chem. A **109**, 4366 (2005).
- ²⁷J. Autschbach, B. A. Hess, M. P. Johansson, J. Neugebauer, M. Patzschke, P. Pyykko, M. Reiher, and D. Sundholm, Phys. Chem. Chem. Phys. 6, 11 (2004).
- ²⁸L. Gagliardi, J. Am. Chem. Soc. **125**, 7504 (2003).
- ²⁹B. Kiran, X. Li, H. J. Zhai, and L. S. Wang, J. Chem. Phys. **125**, 133204 (2006).
- ³⁰B. Kiran, X. Li, H. J. Zhai, L. F. Cui, and L. S. Wang, Angew. Chem., Int. Ed. 43, 2125 (2004).
- ³¹H. J. Zhai, L. S. Wang, D. Y. Zubarev, and A. I. Boldyrev, J. Phys. Chem. A **110**, 1689 (2006).
- ³²Y. Erdogdu, T. Jian, G. V. Lopez, W. L. Li, and L. S. Wang, Chem. Phys. Lett. 610–611, 23 (2014).
- ³³H. J. Zhai, J. Li, and L. S. Wang, J. Chem. Phys. **121**, 8369 (2004).
- ³⁴H. Tanaka, S. Neukermans, E. Janssens, R. E. Silverans, and P. Lievens, J. Chem. Phys. **119**, 7115 (2003).
- ³⁵C. Majumder, A. K. Kandalam, and P. Jena, Phys. Rev. B 74, 205437 (2006).
- ³⁶C. Majumder and S. K. Kulshreshtha, Phys. Rev. B 73, 155427 (2006).
- ³⁷Q. Sun, Q. Wang, G. Chen, and P. Jena, J. Chem. Phys. **127**, 214706 (2007).
- ³⁸M. Walter and H. Häkkinen, Phys. Chem. Chem. Phys. 8, 5407 (2006).
 ³⁹L. M. Wang, S. Bulusu, W. Huang, R. Pal, L. S. Wang, and X. C. Zeng,
- J. Am. Chem. Soc. **129**, 15136 (2007).
- ⁴⁰R. Pal, L. M. Wang, W. Huang, L. S. Wang, and X. C. Zeng, J. Am. Chem. Soc. **131**, 3396 (2009).
- ⁴¹A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997).
- ⁴²D. M. Neumark, J. Phys. Chem. A **112**, 13287 (2008).
- ⁴³I. León, Z. Yang, H. T. Liu, and L. S. Wang, Rev. Sci. Instrum. 85, 083106 (2014).
- ⁴⁴I. León, Z. Yang, and L. S. Wang, J. Chem. Phys. **138**, 184304 (2013).
- ⁴⁵Z. Yang, I. León, and L. S. Wang, J. Chem. Phys. **139**, 021106 (2013).
- ⁴⁶I. León, Z. Yang, and L. S. Wang, J. Chem. Phys. **139**, 089903 (2013).
- ⁴⁷I. León, Z. Yang, and L. S. Wang, J. Chem. Phys. **139**, 194306 (2013).
- ⁴⁸I. León, Z. Yang, and L. S. Wang, J. Chem. Phys. 140, 084303 (2014).
- ⁴⁹L. S. Wang, H. S. Cheng, and J. W. Fan, J. Chem. Phys. **102**, 9480 (1995).
- ⁵⁰V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, Rev. Sci. Instrum. **73**, 2634 (2002).
- ⁵¹G. A. Garcia, L. Nahon, and I. Powis, Rev. Sci. Instrum. 75, 4989 (2004).
- ⁵²J. Clark, S. T. Call, D. E. Austin, and J. C. Hansen, J. Phys. Chem. A **114**, 6534 (2010).
- ⁵³B. B. Averkiev, S. Call, A. I. Boldyrev, L. M. Wang, W. Huang, and L. S. Wang, J. Phys. Chem. A **112**, 1873 (2008).
- ⁵⁴S. T. Call, D. Y. Zubarev, and A. I. Boldyrev, J. Comput. Chem. 28, 1177 (2007).
- ⁵⁵S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science 220, 671 (1983).
- ⁵⁶J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ⁵⁷P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985).
- ⁵⁸J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- ⁵⁹D. Figgen, G. Rauhut, M. Dolg, and H. Stoll, Chem. Phys. **311**, 227 (2005).
- ⁶⁰T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- ⁶¹M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. 108, 4439 (1998).
- ⁶²Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li, and L. S. Wang, Nat. Commun. 5, 3113 (2014).
- ⁶³ M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus *et al.*, Comput. Phys. Commun. **181**, 1477 (2010).
- ⁶⁴X. B. Wang, C. F. Ding, and L. S. Wang, J. Chem. Phys. **110**, 8217 (1999).
- ⁶⁵X. B. Wang, H. K. Woo, and L. S. Wang, J. Chem. Phys. **123**, 051106 (2005).
- ⁶⁶J. Li, X. Li, H. J. Zhai, and L. S. Wang, Science **299**, 864 (2003).
- ⁶⁷H.-J. Zhai, B. Kiran, and L.-S. Wang, J. Chem. Phys. 121, 8231 (2004).
- ⁶⁸X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, and L. S. Wang, Science **291**, 859 (2001).
- ⁶⁹T. Sommerfeld, J. Chem. Phys. 132, 124305 (2010).
- ⁷⁰P. Pyykkö, Chem. Rev. 88, 563 (1988).
- ⁷¹H. Häkkinen, M. Moseler, and U. Landman, Phys. Rev. Lett. **89**, 033401 (2002).
- ⁷²H. Gronbeck and P. Broqvist, Phys. Rev. B **71**, 073408 (2005).
- ⁷³L. M. Wang and L. S. Wang, Nanoscale 4, 4038 (2012).