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Probing the structures and bonding of auropolyynes, Au— $(C \equiv C)_n$ —Au⁻ (*n* = 1–3), using high-resolution photoelectron imaging

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We report an investigation of a series of auropolyynes, $Au-(C\equiv C)_n-Au^-$ (n = 1-3), using highresolution photoelectron imaging and *ab initio* calculations. Vibrationally resolved photoelectron spectra are obtained, allowing the electron affinities of $Au-(C\equiv C)_n$ —Au to be accurately measured as 1.651(1), 1.715(1), and 1.873(1) eV for n = 1-3, respectively. Both the Au-C symmetric stretching and a bending vibrational frequency are observed for each neutral auropolyyne. Theoretical calculations find that the ground state of $Au_2C_2^-$ has a linear acetylenic $Au-C\equiv C-Au^$ structure, whereas the asymmetric $Au-Au-C\equiv C^-$ structure is a low-lying isomer. However, for $Au_2C_4^-$ and $Au_2C_6^-$, our calculations show that the asymmetric $Au-Au-(C\equiv C)_n^-$ isomers are the global minima and the $Au-(C\equiv C)_n-Au^-$ symmetric structures become low-lying isomers. All the asymmetric $Au-Au-(C\equiv C)_n^-$ isomers are found computationally to have much higher electron binding energies and are not accessible at the detachment photon energies used in the current study. For neutral Au_2C_{2n} , the $Au-(C\equiv C)_n-Au$ auropolyyne structures are found to be the global minima for n = 1-3. The electronic structures and bonding for $Au-(C\equiv C)_n-Au$ (n = 1-3) are compared with the corresponding $Au-(C\equiv C)_n$ and $Au-(C\equiv C)_n-H$ species. *Published by AIP Publishing*. https://doi.org/10.1063/1.5040336

I. INTRODUCTION

Linear chains consisting of sp-hybridized carbon atoms (polyynes or cumulenes) have unique electronic and optical properties. They are considered as the ultimate onedimensional quantum wires and have attracted increasing interest in nanoscience.¹ For finite systems, their properties depend on both the chain length and the termini, forming polyynes for an even number of carbon atoms or cumulenes for an odd number of carbon atoms.²⁻⁷ Gold termini are of particular interest because gold is an ideal electrode material. The Au-C chemical bonding is important to understand the conducting properties of the linear carbon chain as a 1D quantum wire. Gold possesses many unusual properties due to the strong relativistic effects.⁸ Specifically, we have found that the gold atom possesses strong capacity to form covalent bonds⁹ and exhibits bonding properties analogous to hydrogen in binary gold clusters with silicon and boron.^{10–15} The Au-C bonding is also important in understanding homogeneous catalysis involving gold.^{16–18} Toward that goal, we have investigated previously a series of Au-alkynyl complexes, $LAuCCH^{-}$ (L = Cl, I, CCH) using photoelectron spectroscopy (PES) and theoretical calculations.¹⁹ We observed an unusually large Au-C stretching frequency in these complexes, leading to the surprising finding that the Au-C bond in these complexes is extremely strong with a calculated dissociation energy of 5.01 eV in ClAuCCH⁻. Even more surprisingly, in Ref. 19, we found that the Au–C single bond in ClAuCCH⁻ is stronger than the Au=C double bond in ClAu=CH₂ and the Au≡C triple bond in ClAu≡C,^{20–23} revealing an inverse correlation between the bond strength and bond orders in the series of Au-C compounds. The auxiliary Cl ligand is found to polarize the Au center in ClAuCCH⁻, resulting in the unusually strong Au-C bond. As a comparison, we have investigated a series of AuC_{2n}⁻ and AuC_{2n}H⁻ species^{24,25} using high-resolution PES based on a velocity-map imaging (VMI) instrument²⁶ and confirmed the strong influence of the auxiliary ligand on the Au-C bonds in LAuCCH⁻. A similar study on AuC₄H⁻,²⁷ as well AuC₂H⁻ and Au₂C₂⁻,²⁸ has recently been reported at lower resolution.

In the current article, we present a study on the electronic structure and chemical bonding in a series of auropolyynes, $Au(C \equiv C)_n Au^-$ (n = 1-3), and their corresponding neutrals

using high-resolution PE imaging and *ab initio* calculations. Vibrationally resolved PE spectra using the VMI instrument are obtained for the ground state detachment transitions of $Au(C \equiv C)_n Au^-$, providing detailed spectroscopic data for the corresponding neutral species. Theoretical calculations show that the linear acetylenic $Au-C \equiv C-Au^{-}$ is the global minimum with the asymmetric linear Au-Au-C2⁻ structure as a low-lying isomer. Surprisingly, the symmetric polyyne-type AuC₄Au⁻ and AuC₆Au⁻ structures are found to be low-lying isomers, whereas their global minima are of the asymmetric Au-Au- C_{2n}^{-} structures. The corresponding neutrals for all three di-gold species possess the polyyne-type linear global minima, $Au(C \equiv C)_n Au$ (*n* = 1–3). Because the electron binding energies of the Au-Au- C_{2n}^{-} structures are very high, the observed PE spectra are all due to the $Au(C \equiv C)_n Au^-$ species, as confirmed by the good agreement between experiment and theory. In addition to accurate electron affinities (EAs), the Au-C stretching frequency and a bending frequency are measured for each AuC_{2n}Au (n = 1-3) auropolyyne. The Au-C bond is found to be relatively strong, with calculated dissociation energies for the AuC_{2n}Au \rightarrow AuC_{2n} + Au channel ranging from 3.52 eV for n = 1 to 3.24 eV for n = 3.

II. EXPERIMENTAL METHOD

The experiment was done using a PE imaging apparatus, equipped with a laser vaporization supersonic cluster source, a time-of-flight mass spectrometer, and a high-resolution VMI lens system.^{26,29–31} A disk target made of graphite and Au (C/Au atom ratio \sim 1/9) was used for laser vaporization with a helium carrier gas seeded with 10% argon, which was shown to produce relatively cold gold cluster anions previously.³² Clusters formed inside the nozzle were entrained by the carrier gas and underwent a supersonic expansion. After a skimmer, anions from the collimated cluster beam were extracted perpendicularly into a time-of-flight mass spectrometer. The Au₂C_{2n}⁻ anionic clusters were mass-selected and focused into a collinear VMI system for photodetachment by a tunable laser. Photoelectrons were accelerated toward a position-sensitive detector with a 75 mm diameter microchannel plate coupled to a phosphor screen and a chargecoupled device (CCD) camera. A National Instrument PXImainframe system was used to control the apparatus and for data acquisition. A high-resolution Continuum Sunlite optical parametric oscillator (OPO) system (linewidth $< 0.3 \text{ cm}^{-1}$) pumped by an injection-seeded Continuum Powerlite laser was used for photodetachment. Typical pulse energies used were $\sim 150 \,\mu$ J. 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. The electron count rates were relatively low for the current experiment, and photoelectron images were averaged between 300 000 and 700 000 laser shots. Inverse-Abel transformation was done to obtain the three-dimensional (3D) electron distributions from the recorded two-dimensional (2D) images using both the BASEX³³ and pBASEX³⁴ programs, which yielded similar results. The PE imaging system was calibrated using the known spectrum of Au⁻.

III. THEORETICAL METHODS AND RESULTS

Density Functional Theory (DFT) calculations were performed on Au₂C_{2n}⁻ (n = 1-3) with the Gaussian 09 program package³⁵ using the B3LYP functional.^{36,37} The allelectron 6-31++G(d,p) basis set³⁸ was used for the carbon atoms, and the Lanl2dz basis set and the associated effective core potential (ECP)³⁹⁻⁴¹ were used for gold during the optimization calculations. Vibrational frequencies were calculated to confirm that the obtained structures were true minima. In addition, wavefunction-based CASSCF/CASPT2 calculations⁴²⁻⁴⁶ were performed including spin-orbit coupling, together with the atomic natural orbital (ANO-RCC) basis sets of triple- ζ size for all atoms.^{47,48} All these calculations were carried out using the MOLCAS 8.0 suite of programs.⁴⁹ The structural parameters of the calculated clusters are given in Fig. 1.

We optimized different types of structures for the Au_2C_{2n} and $Au_2C_{2n}^{-}$ species, and found only the linear/bent Au-Au-C_{2n} and Au-C_{2n}-Au atomic configurations to be relevant. We found that the global minimum of $Au_2C_2^-$ is linear with the Au-C₂-Au configuration both for the anion $(^{2}\Sigma_{u}^{+})$ and neutral $(^{1}\Sigma_{g}^{+})$. For Au₂C₄⁻ and Au₂C₆⁻, we found that the linear Au-Au- C_4^- and Au-Au- C_6^- asymmetric configurations are the global minima (Table I and Fig. 1). The symmetric Au-C₄-Au⁻ and Au-C₆-Au⁻ configurations are slightly bent, and they are about 0.4 eV above the global minima at the B3LYP level of theory. The most stable structures of their corresponding neutrals, however, are of the linear Au– C_4 –Au and Au– C_6 –Au symmetric configurations. The relative energies and selected vibrational frequencies for the two configurations of each species are given in Table I, whereas Fig. 1 shows all the anion and neutral structures along with the relevant bond lengths and angles. For the Au– C_{2n} –Au configurations, there are strong C-C bond length alternations in both the anions and neutrals. Hence, they are all of the polyyne-type and can be written



FIG. 1. Structures and bond lengths of $Au-C_{2n}-Au^{-}$ and $Au-Au-C_{2n}^{-}$ (n = 1-3) and their corresponding neutrals. For each species, the bottom shows the anion structure, while the top structure is for the neutral. All bond distances are given in Å.

TABLE I. Relative energies (ΔE) in eV and vibrational frequencies in cm⁻¹ for the low-frequency modes,^a for Au₂C_{2n}⁻, Au₂C_{2n}, AuC_{2n}Au⁻, and AuC_{2n}Au (*n* = 1–3) calculated by the DFT method using B3LYP and basis set 6-31++g(d,p) for C and Lanl2dz for Au. Values marked by * are calculated by CASSCF/CASPT2 including spin-orbit coupling, together with ANO-RCC basis sets of triple- ζ quality for Au and C. The ΔE values of the neutral species account for the difference between the anion and neutral in the same isomeric configuration.

	ΔΕ	ν_1	v_2	v ₃	ν_4	ν ₅	EA (theoretical)	EA (Expt.) ^b
$\overline{\text{Au-C}_2-\text{Au}^-(\text{D}_{\infty h},^2 \Sigma_u^+)}$	0.00*/0.00	$139(\sigma_g)$	77 (Π _u)	313 (Пд)	$557(\sigma_u)$	$2054(\sigma_g)$		
Au-Au- C_2^- ($C_{\infty v}$, $^2\Sigma$)	0.22*/0.47	136 (o)	57 (II)	408 (П)	421 (o)	1979 (σ)		
Au-C ₂ -Au $(D_{\infty h}, {}^{1}\Sigma_{g}^{+})$	1.32*/1.89	$159(\sigma_g)$	108 (П _u)	263 (Π _g)	$691(\sigma_u)$	$2171(\sigma_g)$	1.32*/1.89	1.651
Au-Au-C ₂ (C _{∞v} , ¹ Σ ⁺)	4.12*/4.87	132 (o)	41 (Π)	445 (П)	455 (σ)	1979 (o)	3.90*/4.40	
Au-Au- C_4^- ($C_{\infty v}$, $^2\Pi$)	0.00*/0.00	143 (σ)	33(П)	101 (П)	148(П)	207 (П)		
$Au - C_4 - Au^- (C_s, {}^2A')$	1.16*/0.35	146 (a')	45 (a')	92 (a'')	367 (a')	422 (a')		
Au-C ₄ -Au $(D_{\infty h}, {}^{1}\Sigma_{g}^{+})$	2.53*/2.34	$142(\sigma_g)$	$56(\Pi_{u})$	167 (Пд)	350 (Π _u)	500 (Пg)	1.37*/1.99	1.715
Au-Au-C ₄ (C _s , $^{1}A'$)	5.04*/4.89	142 (a')	23 (a')	123 (a')	277 (a')	298 (a'')	5.04*/4.89	
$\overline{\text{Au-Au-C}_6^-(\text{C}_{\infty\text{v}},^2\Pi)}$	0.00*/0.00	138 (σ)	20 (II)	72 (II)	190(П)	342 (o)		
$Au - C_6 - Au^- (C_s, {}^2A')$	0.86*/0.40	$120(\sigma_g)$	$32(\Pi_{u})$	80 (Π _g)	225 (Π _u)	346 (Пg)		
Au-C ₆ -Au $(D_{\infty h}, {}^{1}\Sigma_{g}^{+})$	2.43*/2.61	$129(\sigma_g)$	33 (П _u)	109 (П _g)	$213(\Pi_{u})$	370 (Пg)	1.57*/2.21	1.873
Au-Au-C ₆ (C ₁ , ¹ A)	4.79*/4.93	138 (a)	18 (a)	70 (a)	187 (a)	355 (a)	4.79*/4.93	

 $^{a}v_{1}$ —Au—C stretch; v_{2} —bending; v_{3} —bending; v_{4} —bending; v_{5} —bending/stretching. No mixing between the electronic states was observed for any species.

^bExperimental uncertainties were estimated to be ± 0.001 eV.

as Au(C \equiv C)_nAu⁻ and Au(C \equiv C)_nAu (n = 1-3). As shown in Table I, we found that the EAs of the Au-C_{2n}-Au and Au₂-C_{2n} (n = 1-3) configurations are very different with the former having EAs all below 2 eV and the latter all above 4 eV.

We also did Franck-Condon (FC) simulations for detachment transitions from the electronic ground states of $Au-C_{2n}-Au^{-}$ to those of $Au-C_{2n}-Au$ for comparison with the experimental data. The simulations were done using the PESCAL program,⁵⁰ which computes FC factors by numerical integration of vibrational wavefunctions of a properly fitted Morse oscillator.

IV. EXPERIMENTAL RESULTS

The PE images and spectra of $Au_2C_{2n}^-$ at different visible wavelengths are shown in Figs. 2–4 for n = 1-3, respectively. Multiple photon energies are used in order to obtain better resolution for near-threshold features.⁵¹ The detachment energies increase from n = 1 to 3 but are all around 2 eV. Hence, the observed spectra should be all due to the auropolyynes, $Au(C \equiv C)_n Au^-$ (*n* = 1–3), according to the theoretical results. The measured EAs for the three species are indeed in excellent agreement with the theoretical EAs at the B3LYP level for the auropolyynes, as shown in Table I. In the cases of n = 2and 3, the observed spectra are due to the minor auropolyyne isomers. The dominating species in the cluster beam should be the asymmetric Au–Au– C_{2n}^{-} global minima. But their electron binding energies are too high to be accessed at the detachment photon energies used here. Hence, the observed spectra should be due to detachment transitions from the ground electronic state of each $Au(C \equiv C)_n Au^-$ species to that of its corresponding neutral. Rich vibrational features are observed for each species, and the binding energies for all the observed peaks in Figs. 2-4 are given in Tables II-IV, respectively.

A. High-resolution PE imaging and spectra for $Au-C_2-Au^-$

The spectrum of $Au-C_2-Au^-$ in Fig. 2(e) shows a major vibrational progression (labeled as a_1' to d_1'),



FIG. 2. High-resolution PE images and spectra of $Au_2C_2^-$ at photon energies of (a) 1.6578 eV, (b) 1.6850 eV, (c) 1.7018 eV, (d) 1.8146 eV, and (e) 1.9740 eV. The left panels show the PE images after inverse-Abel transformation. The double arrows indicate the laser polarizations.



FIG. 3. High-resolution PE images and spectra of $Au_2C_4^-$ at photon energies of (a) 1.7264 eV, (b) 1.7678 eV, (c) 1.8146 eV, (d) 1.8498 eV, and (e) 2.0002 eV. The left panels show the PE images after inverse-Abel transformation. The double arrows indicate the laser polarizations.

suggesting a significant geometry change between the ground state of Au- C_2 -Au⁻ and that of neutral Au- C_2 -Au. In Fig. 2(d), more fine features are resolved and are labeled as a_2' to h_2' . Each peak beyond the a_1' peak is resolved into a doublet. There is a significant intensity enhancement effect in Fig. 2(d), as shown by the anomalous intensities of peaks f_3' and h_2' . This intensity enhancement could be due to threshold enhancements or suggest that an autodetachment mechanism is being at play. More members of the major vibrational progression are also observed in Fig. 2(d). At even lower photon energies [Figs. 2(a)-2(c)], the fine features are resolved even better, as well as intensity enhancements. The average spacing of the major vibrational progression $a_1'-f_1'$ is about 153 cm⁻¹, and the spacing between the main peak and the following resolved fine feature, for example, from peak a_1' to a_2' , is about 204 cm⁻¹. Hence, the fine features, a_2' , b_2' , etc., should be due to combinational vibrational levels between the most Franck-Condonactive mode of 153 cm^{-1} and another mode of 204 cm^{-1} . The binding energies both in eV and cm^{-1} for all the observed peaks and their assignments are given in Table II for $Au-C_2-Au^-$.

The β values for all the vibrational peaks are negative at low kinetic energies and become almost zero as the kinetic energies of the photoelectrons increase [Fig. 5(a)].



FIG. 4. High-resolution PE images and spectra of $Au_2C_6^-$ at photon energies of (a) 1.8796 eV, (b) 1.9290 eV, (c) 1.9707 eV, (d) 2.1002 eV, and (e) 2.3399 eV. The left panels show the PE images after inverse-Abel transformation. The double arrows indicate the laser polarizations.

B. High-resolution PE imaging and spectra for $Au-C_4-Au^-$

Similar behaviors are observed in the high-resolution PE spectra of $Au-C_4-Au^-$ (Fig. 3). The spectrum in Fig. 3(e)

TABLE II. Observed binding energies from the high-resolution photoelectron spectra of $Au_2C_2^-$ (Fig. 2).

Observed	Binding energies ^a		Peak separation of the main and minor	Assignment	
peaks	eV	cm ⁻¹	progressions (cm ⁻¹)	$(v_1 v_2)$	
a ₁ ′	1.651	13 319		00	
b ₁ ′	1.670	13 471	152	10	
a2′	1.678	13 530	211	02	
c1'	1.690	13 628	157	20	
b2'	1.696	13 678	207	12	
d ₁ ′	1.708	13 777	150	30	
c2'	1.714	13 822	194	22	
e1'	1.727	13 929	152	40	
d2'	1.732	13 972	195	32	
f_1'	1.746	14 081	152	50	
e2'	1.751	14 120	191	42	
f_2'	1.770	14 278	197	52	
e ₃ ′	1.776	14 322	197	44	
f_3'	1.792	14 452	186	54	
h2'	1.807	14 573	191	72	

^aThe peak positions carry an uncertainty of ±0.001 eV.

TABLE III. Observed binding energies from the high-resolution photoelectron spectra of $Au_2C_4^-$ (Fig. 3).

Observed	Binding energies ^a		Peak separation of the main and minor	Assignment
peaks	eV	cm ⁻¹	progressions (cm ⁻¹)	$(v_1 v_2)$
a ₁ ′	1.715	13 834		00
a2′	1.721	13 880	46	01
b ₁ ′	1.733	13 979	145	10
b2'	1.740	14 031	52	11
b3'	1.744	14 064	85	12
c1'	1.751	14 122	143	20
c3'	1.761	14 200	78	22
d ₁ ′	1.768	14 262	140	30
d2'	1.774	14 308	46	31
d3′	1.779	14 351	89	32
e1'	1.786	14 403	141	40
e3'	1.797	14 495	92	42
f_1'	1.804	14 548	145	50
f ₃ ′	1.815	14 636	87	52
g1'	1.821	14 686	138	60
g3'	1.832	14 776	90	62

^aThe peak positions have an uncertainty of ±0.001 eV.

displays a major vibrational progression $(a_1'-g_1')$ with an average spacing of about 142 cm⁻¹. At lower photon energies, significant intensity enhancements are observed, in addition to more fine features due to weak excitations of another low frequency mode, such as a_2' , b_2' , etc., with a frequency of about 45 cm⁻¹. For peaks b_1' , c_1' , and d_1' , a second quantum of the weak mode is observed $[b_3', c_3', and d_3'$ in Fig. 3(c)]. However, for peaks c_1' , e_1' , f_1' , and g_1' of the major progression, only even quantum of the weak modes seems to be observed $[c_3', e_3', f_3', and g_3'$ in Figs. 3(c) and 3(d)]. Some of these fine features are observed more promptly due to the intensity enhancements. The binding energies both in eV and cm⁻¹ of all the observed peaks and their assignments are given in Table III for Au-C₄-Au⁻.

TABLE IV. Observed binding energies from the high-resolution photoelectron spectra of ${\rm Au}_2{\rm C}_6^-$ (Fig. 4).

Observed	Binding energies ^a		Peak separation of the main and minor	Assignment $(v_1 v_5)$
peaks eV	cm ⁻¹	progressions (cm ⁻¹)		
a ₁ '	1.873	15 107		00
b1'	1.888	15 229	122	10
c1'	1.904	15 357	128	20
d ₁ ′	1.920	15 485	128	30
a2′	1.923	15 509	402 (from a ₁ ')	01
e1'	1.935	15 607	122 (from d ₁ ')	40
b ₂ ′	1.938	15 635	126 (from a ₂ ')	11
c2'	1.954	15 759	124	21
d2′	1.969	15 881	122	31
a3′	1.972	15 905	798 (from a ₁ ')	02
b3'	1.986	16 022	117	12
c3'	2.001	16 139	117	22
d3'	2.017	16 268	129	32

^aThe peak positions have an uncertainty of ±0.001 eV.



FIG. 5. Experimental anisotropy parameters (b) of (a) $AuC_2Au^-,$ (b) $AuC_4Au^-,$ and (c) $AuC_6Au^-.$

Similar to the Au–C₂–Au⁻ spectra, the β values for all the vibrational peaks in the spectra of Au–C₄–Au⁻ are negative at low kinetic energies and become almost zero as the kinetic energies of the photoelectrons increase [Fig. 5(b)].

C. High-resolution PE imaging and spectra for $Au-C_6-Au^-$

The spectra of Au—C₆—Au⁻ presented in Fig. 4 are rather congested with increasing vibrational complexity, suggesting excitations of several vibrational modes. There is a clear long vibrational progression with some well-resolved peaks (labeled as $a_1'-e_1'$) and a vibrational spacing of 125 cm⁻¹. On the basis of the accurate peak positions and spacings, two more vibrational progressions, $a_2'-d_2'$ and $a_3'-d_3'$, can be identified with a similar vibrational spacing as the $a_1'-e_1'$ progression. The peaks a_1', a_2' , and a_3' seem to define another vibrational mode with a much higher frequency. Unlike the spectra observed for Au-C₂-Au⁻ and Au-C₄-Au⁻, no pronounced intensity enhancements are observed in the lower photon energy spectra for Au-C₆-Au⁻. The binding energies both in eV and cm⁻¹ of all the observed peaks and their assignments are given in Table IV for Au-C₆-Au⁻.

The β values are zero for low kinetic energies and increase up to 1 as the kinetic energies of the photoelectrons increase [Fig. 5(c)].

V. DISCUSSION

A. $Au-C\equiv C-Au^{-}$ and $Au-C\equiv C-Au$

Figure 6 shows the top three occupied valence molecular orbitals of Au–(C \equiv C)_n–Au⁻ (n = 1–3). Linear structures are used for the MO plots for n = 2 and 3 for the convenience of comparison, even though their true ground states are slightly nonlinear (Fig. 1). For $Au-C_2-Au^-$, the electron detachment should come from the 12σ SOMO (singly occupied molecular orbital), leading to the ${}^{1}\Sigma_{g}{}^{+}$ ground electronic state of the neutral auroacetylene Au-C \equiv C-Au. The 12 σ orbital is a weak Au-C anti-bonding MO, consistent with the fact that the major structural change between the anion and the neutral is the reduction of the Au—C bond length by 0.06 Å (Fig. 1). Hence, the most Franck-Condon-active mode upon electron detachment from $Au-C \equiv C-Au^{-}$ should be the Au-C symmetric stretching. The observed vibrational frequency of 153 cm⁻¹ for the major vibrational progression in the PE spectra of Au-C \equiv C-Au⁻ is in excellent agreement with the calculated stretching frequency of 159 cm⁻¹ for Au−C≡C−Au (Table I). Since both $Au-C \equiv C-Au^{-}$ and $Au-C \equiv C-Au$ are linear with $D_{\infty h}$ symmetry, only even quanta of the bending mode are allowed. The observed vibrational spacing of 204 cm⁻¹ for the weak vibrational features agrees well with the overtone of the calculated 108 cm⁻¹ frequency for the bending mode of Au-C₂-Au, giving rise to an experimentally measured bending frequency of 102 cm⁻¹. Therefore, the peak a_1' in the PE spectra (Fig. 2) represents the 0-0 detachment transition, defining the EA for Au–C₂–Au as 1.651 ± 0.001 eV. The calculated EA of 1.89 eV at the B3LYP level is in good



FIG. 6. The top three valence molecular orbitals of $AuC_{2n}Au^-$ (n = 1-3). In the cases of n = 2 and 3, linear structures are used to plot the MOs.

agreement with the measured value (Table I). The absence of any vibrational hot bands suggests that our cluster beam is quite cold vibrationally.

To further help understand the observed vibrational structures of Au–C₂–Au, we carried out FC simulations, using the Au–C stretching mode and even quanta of the bending mode. The simulated spectrum agrees well with the experiment [Fig. 7(a)], providing credence for the vibrational assignments and the computed structural parameters for Au–C \equiv C–Au and its anion.

B. Au–(C \equiv C)₂–Au⁻ and Au–(C \equiv C)₂–Au

The 16o SOMO of Au-C₄-Au⁻ is also a weak Au-C antibonding orbital (Fig. 6). Electron detachment from the SOMO is expected to result in a shortened Au-C bond length in neutral Au-(C \equiv C)₂-Au, in agreement with the calculated bond length change in the anion and neutral ground states (Fig. 1). Hence, the Au-C stretching mode is expected to be the most Franck-Condon-active mode in the PE spectra, similar to the case of Au−C≡C−Au⁻. The observed frequency of 142 cm⁻¹ for the major vibrational progression is in perfect agreement with the calculated Au-C stretching frequency of 142 cm⁻¹ in Au–(C \equiv C)₂–Au (Table I). Since the Au-(C \equiv C)₂-Au⁻ anion is bent, whereas neutral Au–(C \equiv C)₂–Au is linear, the bending mode is also expected to be active, consistent with the observation of the bending mode in the PE spectra. The observed bending frequency of 45 cm⁻¹ agrees well with the computed bending frequency of 56 cm^{-1} (Table I).

However, the observed bending excitations exhibit some unusual behaviors and seem to depend on the stretching excitation. For low vibrational levels of the stretching mode, peaks a_1', b_1' , and d_1' , corresponding to $v_1 = 0, 1, and 3$, respectively (Fig. 3 and Table III), both odd and even quanta of the bending mode are observed, as expected by the bent structure of $Au - (C \equiv C)_2 - Au^-$. For high vibrational levels of the stretching mode, peaks c_1' , e_1' , f_1' , and g_1' , corresponding to $v_1 = 2$, 4–6, respectively, only even quanta of the bending modes are observed, i.e., c_3' , e_3' , f_3' , and g_3' (Fig. 3 and Table III). In fact, for $v_1 = 2$ (the c_1' peak), even bending excitation is quite weak [peak c_3' in Fig. 3(c)]. In Fig. 3(b), although the c_1' peak is enhanced, there is negligible excitation of the bending mode even near threshold. These are surprising observations, suggesting a complicated potential energy surface and perhaps even vibronic couplings. This conclusion is consistent with the FC simulation [Fig. 7(b)], which displays a poor agreement with the experimental spectrum by only using the stretching mode. Because the anion is slightly bent, some bending activity should be expected. One likely possibility is that the anion has a small barrier to linearity and the zeropoint energy (ZPE) of the bend vibration exceeds the barrier height, resulting in a pseudolinear structure, which could complicate the spectrum. The a_1' peak represents the 0-0 transition in Fig. 3, defining an accurate EA of 1.715 ± 0.001 eV for $Au-C_4-Au$.

C. Au–(C \equiv C)₃–Au[–] and Au–(C \equiv C)₃–Au

Figure 4 shows the PE images and spectra of $Au-C_6-Au^-$ at five photon energies, revealing a more



FIG. 7. Comparison of the calculated Franck-Condon factors for the detachment transitions from (a) AuC₂Au⁻, (b) AuC₄Au⁻, and (c) AuC₆Au⁻ with their corresponding PE spectrum at 1.8146, 2.0002, and 2.3399 eV, respectively. The red vertical lines are the simulated FC factors. The simulations were done using (a) $v_{anion} = 139 \text{ cm}^{-1}$ and $v_{neutral} = 153 \text{ cm}^{-1}$ for the Au-C stretching mode and $v_{anion} = 77 \text{ cm}^{-1}$ and $v_{neutral} = 2 \times 102 \text{ cm}^{-1}$ for the bending mode, and r_{anion} (Au–C) = 2.24 Å for the stretching mode and r_{anion} (Au–C) = 2.14 Å for the bending mode with $r_{neutral}$ (Au–C) = 1.93 Å for both modes. The vibrational temperature was set at 150 K and $\omega_e x_e = 0.5 \text{ cm}^{-1}$, (b) $v_{anion} = 146 \text{ cm}^{-1}$ and $v_{neutral} = 142 \text{ cm}^{-1}$ for the Au–C stretching mode, r_{anion} (Au–C) = 2.11 Å and $r_{neutral}$ (Au–C) = 1.92 Å. The vibrational temperature was set at 150 K and $\omega_e x_e = 0.5 \text{ cm}^{-1}$, (c) v_{anion} = 120 cm⁻¹ and $v_{neutral}$ = 125 cm⁻¹ for the Au–C stretching mode and $v_{anion} = 365 \text{ cm}^{-1} \text{ and } v_{neutral} = 399 \text{ cm}^{-1}$ for the bending mode, r_{anion} $(Au-C) = 2.10 \text{ Å and } r_{neutral} (Au-C) = 1.92 \text{ Å, } r_{anion} (C-C) = 1.28 \text{ Å}$ and $r_{neutral}$ (C–C) = 1.20 Å. The vibrational temperature was set at 150 K and $\omega_e x_e = 0.5 \text{ cm}^{-1}$. Note that for AuC₂Au⁻, we intentionally introduced a displacement in the bending mode, modeled as a 1-D Morse oscillator with only transitions to even quanta, for illustrative purposes of the peak positions. The intensity fitting is artificial, particularly considering that other processes such as autodetachment can be at play.

extensive vibrational progression and increasing vibrational congestion. At the first glance, the spectrum in Fig. 4(e) seems to reveal a vibrational progression with peaks separated by approximately 130 cm⁻¹. However, the intensity variation (peaked at b_3') suggests that there must be more than one mode involved. The a_1' peak should correspond to the 0-0 transition, yielding an accurate EA of 1.873 ± 0.001 eV for Au-C₆-Au and corresponding to the detachment of the electron in the 20σ SOMO (Fig. 6). The main vibrational progression (labeled as a_1', b_1', c_1', \ldots) gives a constant spacing of approximately 125 cm⁻¹, in good agreement with the calculated stretching frequency of 129 cm⁻¹ for the v_1 mode (Table I). On the other hand, this spacing exhibits some variations, in particular, at higher vibrational quanta, suggesting excitations of another mode. For example, peak e_1' in Fig. 4(e) is separated from peak d_1' by 122 cm⁻¹ and has a shoulder on the high binding energy side. When the photon energy is decreased in Figs. 4(c)and 4(d) with higher spectral resolution, peak e_1' is now lower than its shoulder (labeled as b_2'). The presence of a second progression, a_2' , is now clear in Fig. 4(c), where peaks d_1' and a_2' are differentiated. We attribute the b_2' peak to a progression based on the stretching mode starting from the a_2' peak. The c_2' and d_2' peaks also belong to this progression, all separated approximately by 129 cm⁻¹. This second origin, a_2' , is separated by 402 cm⁻¹ from the 0-0 origin, and the third member of this progression, a_3' , is separated by 798 cm⁻¹ from the 0-0 transition. This second active mode with a frequency of $\sim 400 \text{ cm}^{-1}$ is very close to the calculated bending frequency of 370 cm⁻¹ for mode v_5 (Table I). A FC simulation using the v_1 and v_5 modes agrees well with the observed spectra, as shown in Fig. 7(c), providing credence to the assignments.

As shown in Fig. 5(c), the anisotropy parameter is close to zero at low kinetic energies, while it increases at high kinetic energies. The observed *p*-wave character at high kinetic energies is consistent with the σ SOMO of Au–C₆–Au⁻ (Fig. 6) and the fact that no intensity enhancement is observed in the PE spectra (Fig. 4).

D. Comparison of $Au_2C_{2n}^-$ with AuC_{2n}^- and $AuC_{2n}H^-$

We have reported recently a high-resolution PE imaging study on Au C_{2n}^{-} and compared the EAs of Au C_{2n} with those of the corresponding HC_{2n} species.²⁵ We observed a similar EA trend for the aurides and hydrides as the carbon chain length increases: for HC_n , the EAs are 2.969, 3.533, and 3.809 eV for n = 1-3, respectively,⁵²⁻⁵⁴ while the EAs are 3.219, 3.366, and 3.593 eV for AuC₂, AuC₄, and AuC₆, respectively.^{24,25} We observed an approximate increase of about 0.2 eV per C2 unit added to AuC_{2n} . All the values and those obtained in this work are summarized in Table V, together with the observed Au-C stretching frequencies. The observed Au-C stretching and bending modes for $Au-C_{2n}$ -Au are shown in Fig. 8. The obtained EA values in this work are 1.651, 1.715, and 1.873 eV for AuC₂Au, AuC₄Au, and AuC₆Au, respectively. These values show a trend of approximately 0.1 eV per C_2 unit added. It is interesting to compare the EAs between the AuC_{2n}Au and AuC_{2n}H species. Table V shows that replacing the hydrogen by a gold atom in $AuC_{2n}H$ gives similar EAs, further confirming the analogy between hydrogen and gold.^{10–15}

TABLE V. Comparison of the electron affinities (EAs) and Au–C vibrational frequencies in Au–(C \equiv C)_n, Au–(C \equiv C)_n-H, and Au–(C \equiv C)_n-Au (*n* = 1–3).

	EA (eV)	$v_{Au-C} (cm^{-1})$
$Au-C \equiv C (C_s, {}^2A')^a$	3.2192 ± 0.0007	497
Au-(C=C) ₂ $(C_{\infty v}, {}^{2}\Pi_{3/2})^{b}$	3.366 ± 0.001	339
Au–(C \equiv C) ₃ (C _{∞v} , ² $\Pi_{3/2}$) ^b	3.593 ± 0.001	263 ± 6
$Au-C \equiv C-H (C_{\infty y}, {}^{1}\Sigma^{+})^{b}$	1.4747 ± 0.0007	525 ± 8
Au-(C \equiv C) ₂ -H (C _{∞v} , ¹ Σ ⁺) ^b	1.778 ± 0.001	337 ± 8
Au–(C \equiv C) ₃ –H (C _{∞v} , ¹ Σ ⁺) ^b	1.962 ± 0.001	260 ± 8
$Au-C \equiv C-Au (D_{\infty h}, {}^{1}\Sigma_{g}^{+})^{c}$	1.651 ± 0.001	153 ± 9
Au-(C=C) ₂ -Au $(D_{\infty h}, \tilde{1}\Sigma_g^+)^c$	1.715 ± 0.001	142 ± 9
Au-(C \equiv C) ₃ -Au (D _{∞h} , ¹ Σ_g^+) ^c	1.873 ± 0.001	125 ± 11

^aFrom Ref. 24.

^bFrom Ref. 25.

^cCurrent work.

E. Chemical bonding: $AuAu-C_{2n}^{-}$ vs. $CIAu-CCH^{-}$ and $Au-C_{2n}Au$ vs. $H-C_{2n}Au$

Table VI shows the calculated bond dissociation energies of Au— $C_{2n}Au^-$ and AuAu— C_{2n}^- . The Au—C bond strength in Au C_{2n} —Au⁻ (\rightarrow Au C_{2n}^- + Au) is found to decrease from 2.15 eV for n = 1 to 1.57 eV for n = 3. Most surprisingly, we find that the Au—C bond strength in AuAu— C_{2n}^- (\rightarrow Au₂ + C_{2n}^-) is much higher and increases with *n* from 2.73 eV for n = 1 to 3.82 eV for n = 3. Hence, the terminal gold atom plays the role of an auxiliary ligand that polarizes the second Au atom and enhances its bonding with carbon, similar to the Cl ligand in ClAu—CCH⁻. The auxiliary Cl ligand significantly enhances the Au—C bond, resulting in unusually large calculated Au—C bond energies of 4.52 eV and 5.23 eV for ClAu—CCH⁻ (\rightarrow ClAu + CCH⁻) and ClAu—CCH⁻ (\rightarrow ClAu⁻ + CCH), respectively.¹⁹



FIG. 8. The observed stretching and bending normal modes of vibration for auro-polyynes, $AuC_{2n}Au$ (n = 1-3).

TABLE VI. Calculated dissociation energies in eV for two dissociation channels of $AuC_{2n}Au^-$.

	$\operatorname{AuC}_{2n}\operatorname{Au}^{-} \to \operatorname{AuC}_{2n}^{-} + \operatorname{Au}$	$AuAuC_{2n}^{-} \rightarrow C_{2n}^{-} + Au_2$
1	2.152	2.733
2	2.044	2.809
3	1.567	3.817

TABLE VII. Calculated dissociation energies in eV for the neutral $AuC_{2n}Au$ and AuC_nH species.

	$\operatorname{AuC}_{2n}\operatorname{Au} \to \operatorname{AuC}_{2n} + \operatorname{Au}$	$\operatorname{AuC}_{2n}\operatorname{H} \to \operatorname{AuC}_{2n} + \operatorname{H}$
1	3.518	5.150
2	3.349	4.582
3	3.235	4.058

Table VII shows the computed dissociation energies of the neutral AuC_{2n}—Au (\rightarrow AuC_{2n} + Au) and AuC_{2n}—H (\rightarrow AuC_{2n} + H). First, we note that the Au—C bond in AuC_{2n}Au is much stronger than that in the $AuC_{2n}Au^{-}$ anions. Recall that in the latter species, the SOMO is Au-C anti-bonding, which becomes the LUMO in the neutral species (Fig. 6), revealed by the significant Au-C bond length change between the anion and the neutral (Fig. 1). This reflects in the H-C bond strength in AuC_{2n} —H, which is considerably higher than that of the Au-C bond by approximately 1.5 eV. On the other hand, the H-C bond strength strongly depends on the chain length, decreasing by ~0.55 eV per C₂ unit to 4.058 eV in AuC_{2n}—H, whereas the Au-C bond strength in AuC_{2n}-Au only weakly depends on the carbon chain length, decreasing by about 0.1 eV per C₂ unit. The decrease in the Au-C bond strength with n is also reflected in the decreasing Au-C symmetric stretching frequency (Table V).

VI. CONCLUSIONS

We report a high-resolution photoelectron imaging study of a series of auropolyynes $AuC_{2n}Au^{-}$ (n = 1-3) at several photon energies. Vibrationally resolved photoelectron spectra are obtained for the detachment transitions from the ground state of the auropolyyne anions to that of the corresponding neutrals. Vibrational features due to the Au-C symmetric stretching mode and a bending mode are observed for each species. Theoretical calculations show that the ground state of $Au_2C_2^-$ has the $Au-C_2-Au^-$ configuration, but the global minima of $Au_2C_4^-$ and $Au_2C_6^-$ have the asymmetric Au-Au- C_4^- and Au-Au- C_6^- configurations with the AuC_{2n}Au⁻ auropolyyne configurations being higher energy isomers. However, the asymmetric configurations of Au₂C_{2n}⁻ all have much higher electron detachment energies and are not accessible at the low photon energies used in the current photoelectron imaging experiment. The electron affinities for the Au— C_{2n} —Au (n = 1-3) auropolyynes are measured to be 1.651(1), 1.715(1), and 1.873(1) eV, respectively. The Au-C stretching and bending frequencies for AuC₂Au are measured to be 153 and 102 cm⁻¹, respectively. For Au–C₄–Au, we measure an Au-C stretching frequency of 142 cm⁻¹ along with a bending frequency of 45 cm^{-1} . The PE spectra of Au—C₆—Au⁻ reveal complicated and congested vibrational structures. A ground state Au—C stretching frequency of 125 cm⁻¹ is measured definitively with a tentative identification of a high frequency bending mode of 402 cm⁻¹. The SOMO of all auropolyyne anions involve weak Au—C antibonding interactions, resulting in a weaker Au—C bond in the anions and extensive Au—C stretching vibrations in the PE spectra.

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