

PAPER



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Transition from exohedral to endohedral structures of AuGe_n^- ($n = 2-12$) clusters: photoelectron spectroscopy and *ab initio* calculations†

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Gold-doped germanium clusters, AuGe_n^- ($n = 2-12$), were investigated by using anion photoelectron spectroscopy in combination with *ab initio* calculations. Their geometric structures were determined by comparison of the theoretical calculations with the experimental results. The results show that the most stable isomers of AuGe_n^- with $n = 2-10$ are all exohedral structures with the Au atom capping the vertex, edge or face of Ge_n clusters, while AuGe_{11}^- is found to be the critical size of the endohedral structure. Interestingly, AuGe_{12}^- has an I_h symmetric icosahedral structure with the Au atom located at the center. The molecular orbital analysis of the AuGe_{12}^- cluster suggests that the interactions between the 5d orbitals of the Au atom and the 4s4p hybridized orbitals of the Ge atoms may stabilize the I_h symmetric icosahedral cage and promote the Au atom to be encapsulated in the cage of Ge_{12} . The NICS(0) and NICS(1) values are calculated to be -143.7 ppm and -36.3 ppm, respectively, indicating that the icosahedral AuGe_{12}^- cluster is significantly aromatic.

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1. Introduction

Similar to silicon, germanium is an important element in the field of semiconductor materials and the microelectronic industry because of its excellent electron and hole mobilities.^{1,2} Germanium clusters have been investigated previously using experiments and theoretical calculations.³⁻⁷ The structures and properties of transition metal (TM)-doped germanium clusters were also investigated extensively using theoretical calculations and experiments.⁸⁻²¹ The studies show that the doping of TM atoms can stabilize germanium cage structures and may induce novel properties such as a large HOMO–LUMO gap, special spin states, and different charge transfer directions.⁸⁻¹⁸ Thus, the TM-doped germanium clusters may be used as building-blocks for cluster-assembled nanomaterials with special electronic and magnetic properties.

Gold has large electronegativity and high electron affinity. It has been manifested that the relativistic effects can lead to the

relativistic radial contraction and energetic stabilization of the s and p shells of the Au atom, also resulting in the relativistic radial expansion and energetic destabilization of its d and f shells.²² Therefore, the chemical and physical properties of Au-doped germanium clusters would be different from those of the first or second row TM-doped germanium clusters in which the relativistic effects are weaker. It has been found half a century ago that gold-doped germanium can be used to produce an infrared high-frequency photodetector²³ due to its high charge carrier mobility and long wavelength response. It has also been suggested that gold-doped germanium films can be used for fabrication of thermopiles in some types of micro-sensors²⁴ and for ultralow mass highly sensitive cryogenic phonon sensors²⁵ because of their high thermoelectric power and hot electron effects. The synthesis and characterization of Au–Ge clusters showed that the chemistry of metalloid Group 14 cluster compounds can open the way to fabricate new and unusual nanomaterials.^{26,27} Very recently, an atom-thin, ordered and two-dimensional multi-phase germanene film, akin to graphene and silicene, has been successfully synthesized using a gold surface as the substrate,²⁸ but the microscopic details or mechanism of the catalytic processes on the Au surface were not elucidated.

Investigating the structural evolution and electronic properties of Au-doped germanium clusters not only can gain insight into their bonding nature and spectroscopic properties, but also can

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provide valuable information about developing cluster-assembled materials as well as about their potential applications in the microelectronic industry and the catalytic field. The structures of Au-doped germanium clusters were investigated previously using several theoretical calculations,^{29–34} while experimental studies are very rare. In order to get more information regarding the structural evolution and electronic properties of AuGe_n^- clusters, in this work, we investigated AuGe_n^- ($n = 2–12$) clusters using anion photoelectron spectroscopy in combination with *ab initio* calculations. In particular, the structure of AuGe_{12}^- is found to be an I_h symmetric icosahedron, which is different from the structures predicted by previous theoretical studies^{31,32} and also different from the structures of MGe_{12} ($M = \text{V}, \text{Mn–Zn}, \text{and W}$) clusters reported in the literature.^{10–14,16,18,21}

2. Experimental and theoretical methods

2.1 Experimental method

The experiments were conducted on home-built apparatus consisting of a laser vaporization supersonic cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere.³⁵ Briefly, the AuGe_n^- clusters were produced using the laser vaporization source by focusing a pulsed laser beam (532 nm) onto a rotating and translating Au/Ge mixture disk target (13 mm diameter, Au/Ge molar ratio 1/4), while helium gas with ~ 4 atm backing pressure was allowed to expand through a pulsed valve (General Valve Series 9) into the source to cool the formed clusters. The generated cluster anions were mass-analyzed using the time-of-flight mass spectrometer. The cluster anions of interest were selected with a mass gate, decelerated by a momentum decelerator, and then crossed with the fourth harmonic light (266 nm) of another Nd:YAG laser (Continuum Surelite II-10) in the photodetachment region. The photodetached electrons were energy-analyzed using the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated with the known spectra of Cu^- and Au^- recorded under similar conditions. The resolution of the magnetic-bottle photoelectron spectrometer was approximately 40 meV at an electron kinetic energy of 1 eV.

2.2 Theoretical method

The structural optimizations and frequency calculations were carried out using density-functional theory (DFT) with Becke's three-parameter and Lee–Yang–Parr's gradient-corrected correlation hybrid functional (B3LYP)^{36,37} as implemented in the GAUSSIAN 09 program package.³⁸ Pople's all-electron 6-311+G(d) basis set was used for the Ge atoms and the scale relativistic effective core potential Stuttgart/Dresden (SDD) basis set³⁹ was used for the Au atom. No symmetry constraint was imposed during the geometry optimizations. The spin singlet states of AuGe_n^- anions and doublet states of their corresponding neutral molecules were considered during the calculations. Harmonic vibrational frequencies were calculated to confirm that the optimized

structures are real local minima on the potential energy surfaces. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutral molecules and anions, both at the geometries of anionic species. The theoretical adiabatic detachment energies (ADEs) were calculated as the energy differences between the neutral molecules and anions with the neutral molecules relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures. In order to obtain more accurate relative energies, the single-point energies of AuGe_n^- clusters were calculated by using the couple-cluster method including single and double excitations (CCSD)⁴⁰ with the aug-cc-pVTZ-PP basis set⁴¹ for the Au atom and the cc-pVDZ-PP basis set⁴² for the Ge atoms. The zero-point energy (ZPE) corrections were included for all the calculated energies.

3. Experimental results

The photoelectron spectra of AuGe_n^- ($n = 2–12$) clusters recorded using 266 nm photons are presented in Fig. 1. The VDEs and ADEs of these clusters estimated from the photoelectron spectra are listed in Table 1. The VDEs were estimated from the maxima of the first peaks. The ADE of each anionic cluster was determined by drawing a straight line along the

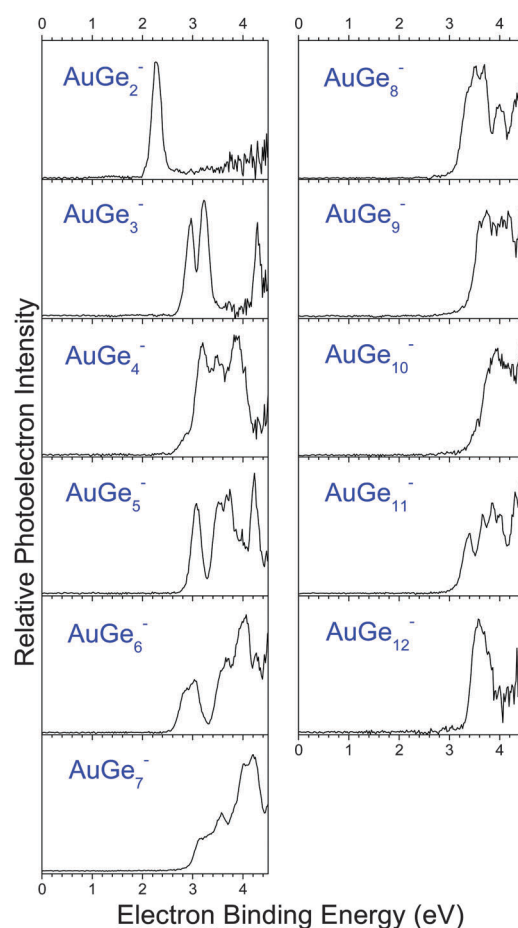


Fig. 1 Photoelectron spectra of AuGe_n^- ($n = 2–12$) clusters recorded with 266 nm photons.

Table 1 Experimental VDEs and ADEs of AuGe_n^- ($n = 2-12$) clusters estimated from their photoelectron spectra

AuGe_n^-	VDE (eV)	ADE (eV)
2	2.27 ± 0.08	2.07 ± 0.08
3	2.97 ± 0.08	2.74 ± 0.08
4	3.17 ± 0.08	2.88 ± 0.08
5	3.08 ± 0.08	2.86 ± 0.08
6	2.87 ± 0.08	2.60 ± 0.08
7	3.14 ± 0.08	2.91 ± 0.08
8	3.37 ± 0.08	3.11 ± 0.08
9	3.60 ± 0.08	3.38 ± 0.08
10	3.55 ± 0.08	3.30 ± 0.08
11	3.40 ± 0.08	3.11 ± 0.08
12	3.60 ± 0.08	3.30 ± 0.08

leading edge of the first peak to cross the baseline of the spectrum and adding the instrumental resolution to the electron binding energy (EBE) value at the crossing point.

The photoelectron spectrum of AuGe_2^- has a sharp peak centered at 2.27 eV. In the spectrum of AuGe_3^- , there are three peaks centered at 2.97, 3.23, and 4.29 eV, respectively. As for the spectrum of AuGe_4^- , it possesses three major peaks centered at 3.17, 3.48, and 3.87 eV, followed by a tailed peak centered at 2.80 eV. The spectrum of AuGe_5^- has four major peaks centered at 3.08, 3.53, 3.75, and 4.23 eV, followed by a shoulder between 3.53 and 3.75 eV. The spectrum of AuGe_6^- shows five peaks centered at 2.87, 3.03, 3.68, 4.07, and 4.27 eV, respectively. For AuGe_7^- , there are four barely discernible peaks centered at 3.14, 3.58, 4.02, and 4.14 eV, respectively. The spectrum of AuGe_8^- has four peaks centered at 3.53, 3.68, 4.00, and 4.45 eV, along with a shoulder centered at 3.37 eV. The spectrum of AuGe_9^- has a peak centered at 3.60 eV, followed by some undistinguished peaks at higher EBE regions. A small peak centered at 3.55 eV can be observed in the spectrum of AuGe_{10}^- , followed by a broad peak centered at 3.94 eV. The spectrum of AuGe_{11}^- has six peaks centered at 3.40, 3.67, 3.86, 4.01, 4.31, and 4.43 eV, respectively. For the spectrum of AuGe_{12}^- , a broad peak centered at 3.60 eV and the onset of a higher EBE peak above 4.0 eV can be observed.

4. Theoretical results

The optimized geometries of the low-lying isomers of AuGe_n^- ($n = 2-12$) clusters are displayed in Fig. 2 with the most stable structures on the left. The relative energies, theoretical VDEs and ADEs of these low-lying isomers are listed in Table 2, along with the experimental VDEs and ADEs for comparison. We also simulated the photoelectron spectra of the low-lying isomers based on theoretically generalized Koopman theorem (GKT).^{43,44} In the simulated photoelectron spectra, the peak of each transition corresponds to the removal of an electron from an individual molecular orbital of the cluster anion. We set the first peak associated with the HOMO to the position of calculated VDE of each isomer, and then shifted the other peaks associated with the deeper orbitals according to their relative energies compared to the HOMO. For convenience, we call the simulated spectra as the density of states (DOS) spectra.

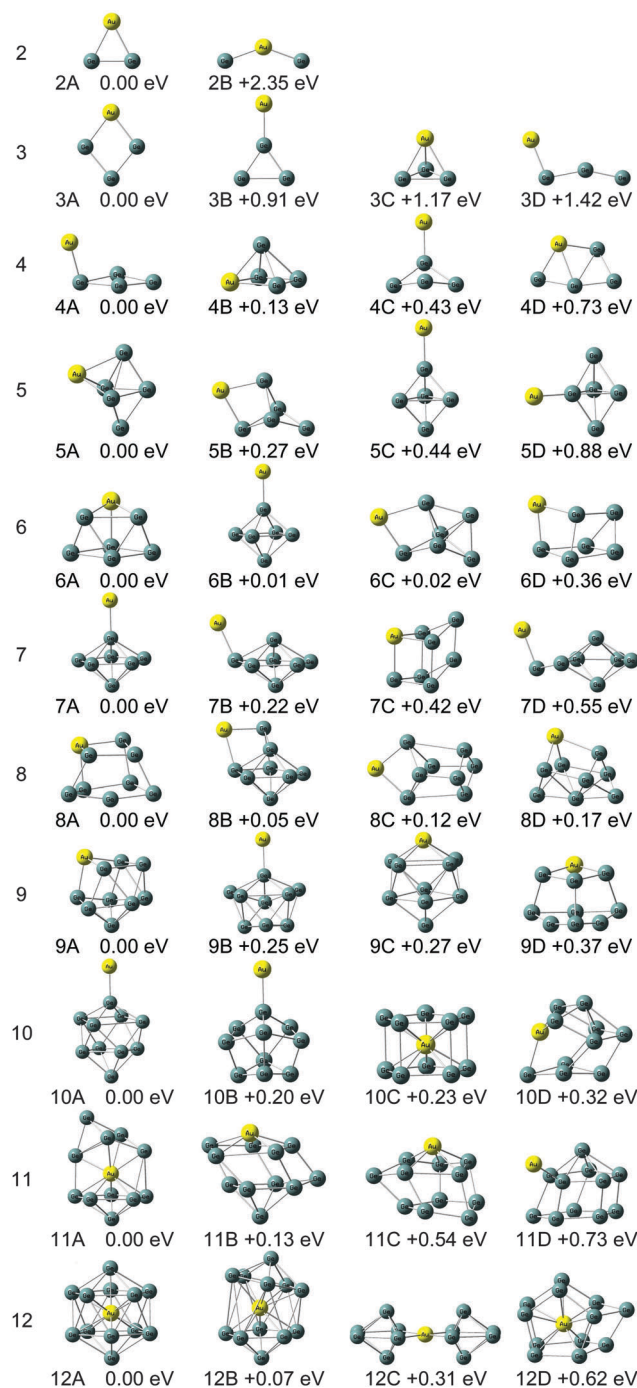


Fig. 2 Geometries of the typical low-lying isomers of AuGe_n^- ($n = 2-12$) clusters optimized at the B3LYP/SDD/Au/6-311+G(d)/Ge level of theory. The energies relative to the most stable isomers are calculated at the CCSD/aug-cc-pVTZ-PP/Au/cc-pVDZ-PP/Ge level of theory.

A comparison of the simulated DOS spectra and experimental spectra is displayed in Fig. 3. More information of isomers can be found in the ESI.†

4.1 AuGe_2^-

The most stable isomer of AuGe_2^- (2A) is an isosceles triangle structure with C_{2v} symmetry. The calculated VDE of 2A is 2.26 eV,

Table 2 Relative energies, theoretical VDEs and ADEs of the low-lying isomers of AuGe_n^- ($n = 2-12$) clusters, as well as the experimental VDEs and ADEs estimated from their photoelectron spectra. The isomers labeled in bold are the most probable isomers in the experiments

Isomer	Sym.	ΔE^a (eV)	VDE (eV)		ADE (eV)		Isomer	Sym.	ΔE^a (eV)	VDE (eV)		ADE (eV)			
			Theo. ^b	Expt.	Theo. ^b	Expt.				Theo. ^b	Expt.	Theo. ^b	Expt.		
AuGe ₂ [−]	2A	C _{2v}	0.00	2.26	2.27	2.06	2.07	AuGe ₈ [−]	8A	C _s	0.00	3.13	3.37	3.02	3.11
	2B	C _{2v}	2.35	1.74		1.73			8B	C ₁	0.05	3.10		2.91	
AuGe ₃ [−]	3A	C _{2v}	0.00	3.08	2.97	2.68	2.74		8C	C _{2v}	0.12	3.32		3.06	
	3B	C _{2v}	0.91	2.70		1.92			8D	C _s	0.17	3.05		2.93	
	3C	C ₁	1.17	2.03		1.90			AuGe ₉ [−]	9A	C ₁	0.00	3.50	3.60	3.31
AuGe ₄ [−]	3D	C _s	1.42	2.53		2.23			9B	C _s	0.25	3.40		3.35	
	4A	C ₁	0.00	3.02	3.17	2.79	2.88		9C	C _s	0.27	3.21		2.92	
	4B	C _s	0.13	2.70		2.49			9D	C _s	0.37	2.99		2.82	
	4C	C _s	0.43	3.07		2.80		AuGe ₁₀ [−]	10A	C ₁	0.00	3.63	3.55	3.36	3.30
	4D	C ₁	0.73	2.27		2.18			10B	C _s	0.20	3.48		3.24	
AuGe ₅ [−]	5A	C ₁	0.00	2.91	3.08	2.70	2.86		10C	D _{5h}	0.23	3.13		3.00	
	5B	C _{2v}	0.27	3.21		2.61			10D	C ₁	0.32	3.42		2.76	
	5C	C _{3v}	0.44	3.33		3.12		AuGe ₁₁ [−]	11A	C _s	0.00	3.48	3.40	3.29	3.11
	5D	C _{2v}	0.88	3.06		2.77			11B	C ₁	0.13	3.26		3.04	
AuGe ₆ [−]	6A	C ₁	0.00	2.65	2.87	2.48	2.60		11C	C ₁	0.54	3.37		3.17	
	6B	C _{4v}	0.01	3.34		2.85			11D	C ₁	0.73	3.18		2.90	
	6C	C _s	0.02	2.98		2.81		AuGe ₁₂ [−]	12A	I _h	0.00	3.39	3.60	3.02	3.30
	6D	C ₁	0.36	2.76		2.64			12B	C ₁	0.07	3.60		3.20	
	AuGe ₇ [−]	7A	C _{5v}	0.00	3.42	3.14	3.17	2.91		12C	D ₂	0.31	3.78		3.38
7B		C _s	0.22	3.16		2.86			12D	C ₁	0.62	2.92		2.82	
7C		C _s	0.42	2.96		2.50									
7D		C ₁	0.55	3.12		2.96									

^a The ΔE values are calculated at the CCSD/aug-cc-pVTZ-PP/Au/cc-pVDZ-PP/Ge level of theory. ^b The ADEs and VDEs are calculated at the B3LYP/SDD/Au/6-311+G(d)/Ge level of theory.

in excellent agreement with the experimental value (2.27 eV). As we can see from Fig. 3, the simulated DOS spectrum of isomer 2A fits the experimental spectrum of the AuGe_2^- cluster very well. Therefore, we suggest that isomer 2A is the most probable one detected in our experiments and isomer 2B can be ruled out because its energy is much higher than 2A by 2.35 eV.

4.2 AuGe_3^-

The lowest-lying isomer of AuGe_3^- (3A) is a rhombus structure with C_{2v} symmetry. The calculated VDE of isomer 3A (3.08 eV) is very close to the experimental value (2.97 eV), and the simulated DOS spectrum of 3A is consistent with the experimental spectrum. Thus, we suggest that isomer 3A is the most likely structure observed in our experiments. Isomers 3B, 3C, and 3D can be excluded because they are much less stable than 3A in energy by at least 0.91 eV.

4.3 AuGe_4^-

As for AuGe_4^- , the lowest-lying isomer (4A) can be obtained by the Au atom attached to the top left of the Ge_4 rhombus. Isomer 4B is a compressed tetragonal pyramid structure with the Au atom located at the bottom. The calculated VDE of isomer 4A (3.02 eV) is in good agreement with the experimental measurement (3.17 eV) and its simulated DOS spectrum reproduces the experimental spectrum of AuGe_4^- very well except for the tailed peak centered at 2.80 eV, which could be attributed to the contribution from isomer 4B (VDE: 2.70 eV). Therefore, we suggest isomers 4A and 4B coexist in our experiments, while isomers 4C and 4D can be ruled out because they are much less stable than isomer 4A in energy by at least 0.43 eV.

4.4 AuGe_5^-

With respect to AuGe_5^- , isomer 5A possesses a Ge_5 trigonal bipyramid subunit with the Au atom attached to the top left of the Ge_5 subunit. Isomer 5B can be obtained from isomer 4A by putting an additional Ge atom on the top right of the center of the Ge_4 rhombus. Although the calculated VDEs of isomers 5A, 5C, and 5D (2.91, 3.33, and 3.06 eV) are all in reasonable agreement with the experimental value (3.08 eV), the existence of isomers 5C and 5D can be ruled out because they are much less stable than isomer 5A in energy by at least 0.44 eV. As we can see from Fig. 3, the simulated DOS spectrum of isomer 5A fits the experimental spectrum very well. The DOS spectrum of isomer 5B is similar to the experimental spectrum in some aspects and the calculated VDE (3.21 eV) is also in reasonable agreement with the experimental value; its energy is slightly higher than 5A by 0.27 eV. Therefore, we suggest isomer 5A to be the most probable structure detected in our experiments and the existence of isomer 5B cannot be ruled out.

4.5 AuGe_6^-

The lowest-lying isomer of AuGe_6^- (6A) can be viewed as the Au atom capping the face of the Ge_6 face-capped trigonal bipyramid. Isomer 6B is of C_{4v} symmetry with the Au atom adsorbed onto one Ge atom of the Ge_6 tetragonal bipyramid. Isomer 6C can be considered as derived from isomer 5B by putting an additional Ge atom on the top right of the center of the Ge_4 rhombus. The calculated VDEs of isomers 6A and 6C (2.65 and 2.98 eV) are both in reasonable agreement with the experimental value (2.87 eV), and the combination of their simulated DOS spectra can reproduce the experimental

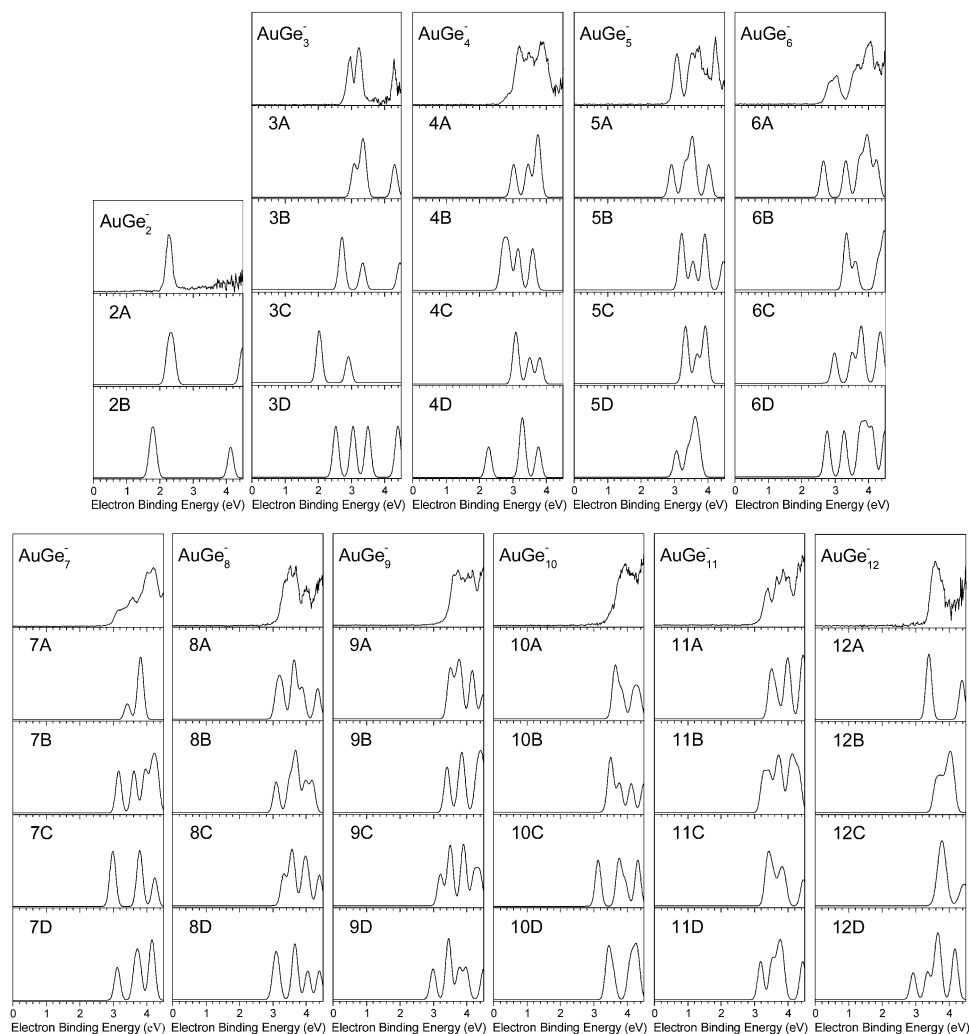


Fig. 3 Comparison between the experimental photoelectron spectra and the simulated DOS spectra of the low-lying isomers of AuGe_n^- ($n = 2-12$) clusters. The simulated spectra were obtained by fitting the distribution of the transition lines with unit area Gaussian functions of 0.20 eV full width at half maximum.

spectrum very well. The energy of isomer 6B is higher than 6A by only 0.01 eV. Although the calculated VDE of isomer 6B (3.34 eV) is much deviated from the experimental value, it may make some contributions to the higher EBE regions. Therefore, we suggest that isomers 6A, 6B, and 6C coexist in our experiments, while isomer 6D can be ruled out because it is much less stable than 6A in energy by 0.36 eV.

4.6 AuGe_7^-

In the structures of AuGe_7^- , isomers 7A and 7B both have a Ge_7 pentagonal bipyramid unit with the Au atom connected to different positions of the Ge_7 unit. The calculated VDE of 7A (3.42 eV) is slightly higher than the experimental result (3.14 eV), and that of 7B (3.16 eV) is in excellent agreement with the experimental value. As we can see from Fig. 3, the combination of simulated spectra of isomers 7A and 7B can fit the experimental spectrum very well. As a result, we suggest that isomers 7A and 7B coexist in our experiments, and isomer 7B may make major contribution to the lower and higher EBE sides.

Besides, isomers 7C and 7D are much higher than 7A in energy by at least 0.42 eV, indicating that their existence can be excluded.

4.7 AuGe_8^-

With regard to AuGe_8^- , the most stable isomer (8A) can be obtained by an additional Ge atom capping the Ge–Ge bond of isomer 7C. The metastable one, 8B can be regarded as the Au atom and one Ge atom face-capping the Ge_7 pentagonal bipyramid, which can also be viewed as an additional Ge atom capping the face of isomer 7B. Isomer 8C can be viewed as the Au atom capping the face of the closely packed Ge_8 tetragonal prism. The calculated VDEs of 8A, 8B, and 8C (3.13, 3.10, and 3.32 eV) are all in reasonable agreement with the experimental value (3.37 eV). Besides, isomers 8B and 8C are energetically close to 8A (higher than 8A in energy by only 0.05 and 0.12 eV, respectively) and their simulated DOS spectra can also duplicate the features of the photoelectron spectrum of AuGe_8^- . Even though isomer 8D is slightly higher than 8A in energy by 0.17 eV, the calculated VDE (3.05 eV) is much smaller than

the experimental value so that its existence can be ruled out. Taking all the above into consideration, we suggest that isomers 8A, 8B and 8C are the dominant structures that contributed to the photoelectron spectrum of AuGe_8^- .

4.8 AuGe_9^-

As for the AuGe_9^- cluster, the lowest-lying isomer (9A) is a multi-rhombus prism with two side-capped Ge atoms, which can be obtained by adding an additional Ge atom face-capping the bottom of isomer 8A. Isomer 9B can be described as the Au atom connecting to one Ge atom of the Ge_9 tricapped trigonal prism (TTP) structure. The calculated VDE of isomer 9A (3.50 eV) is in good agreement with the experimental value (3.60 eV), and its simulated DOS spectrum fits the experimental spectrum very well. Therefore, we suggest that isomer 9A is the most probable structure detected in our experiments. However, the existence of isomer 9B cannot be ruled out because the calculated VDE of isomer 9B (3.40 eV) is in reasonable agreement with the experimental value and its energy is slightly higher than 9A by 0.25 eV. Isomer 9C can be ruled out because its calculated VDE (3.21 eV) deviated much from the experimental value, and isomer 9D can be ruled out because its energy is much higher than isomer 9A by 0.37 eV.

4.9 AuGe_{10}^-

The lowest-lying isomer of AuGe_{10}^- (10A) is a bicapped tetragonal antiprism with the Au atom adsorbed onto one of the two-capped Ge atoms. Isomer 10B can be regarded as derived from isomer 9B by adding an additional Ge atom to the bottom. The calculated VDEs of isomers 10A (3.63 eV) and 10B (3.48 eV) are both in good agreement with the experimental value (3.55 eV). The simulated DOS spectrum of isomer 10A fits the experimental spectrum very well; that of isomer 10B is also similar to the experimental spectrum and its energy is slightly higher than 10A by 0.20 eV. Thus, we suggest that isomer 10A is the most probable structure detected in our experiments and isomer 10B may make some contribution to the broad peak of the photoelectron spectrum of AuGe_{10}^- . Isomers 10C and 10D can be excluded because the calculated VDE of 10C (3.13 eV) deviated much from the experimental value and the energy of 10D is much higher than 10A by 0.32 eV.

4.10 AuGe_{11}^-

As for the ground state, isomer 11A is an endohedral structure with the Au atom completely encapsulated in the Ge_{11} cage consisting of one trigonal bipyramid and one pentagonal pyramid. Isomer 11B can be constructed by the Au atom capping the pentagonal face of the Ge_{11} capped pentagonal antiprism. The calculated VDEs of isomers 11A (3.48 eV) and 11B (3.26 eV) are both in good agreement with the experimental value (3.40 eV), and isomer 11B is slightly higher than 11A in energy by 0.13 eV. Moreover, the combined simulated DOS spectra of isomers 11A and 11B fit the experimental spectrum very well. Therefore, we suggest that isomers 11A and 11B coexist in our experiments. Isomers 11C and 11D can be ruled

out because they are much higher than isomer 11A in energy by at least 0.54 eV.

4.11 AuGe_{12}^-

The lowest-lying isomer of AuGe_{12}^- (12A) is an I_h symmetric icosahedral structure with the Au atom located at the center and twelve Ge atoms situated at its icosahedral vertices. Isomer 12B is a distorted icosahedral structure. The calculated VDE of 12A (3.39 eV) is in reasonable agreement with the experimental value (3.60 eV) and that of 12B (3.60 eV) is equivalent to the experimental value, and the energy of 12B is higher than 12A by only 0.07 eV. As we can see from Fig. 3, the combination of simulated DOS spectra of isomers 12A and 12B can reproduce the experimental spectrum very well. Therefore, we suggest that both isomers 12A and 12B contribute to the experimental spectrum of AuGe_{12}^- . Isomers 12C and 12D are much less stable than isomer 12A in energy by at least 0.31 eV, indicating that their existence can be ruled out.

We have conducted additional calculations on AuGe_{10-12}^- clusters at different levels of theory and the results are presented in the ESI.† We would like to point out that the calculations at different levels of theory lead to the different energetic ordering of isomers, especially for the AuGe_{12}^- cluster. Therefore, it is difficult for us to determine which isomer is the most probable one in the experiment solely by their total energies. Thus, we evaluated the theoretical results by considering both the relative energies and the comparison of the DOS spectra with the experimental spectra. We found that the results obtained from the CCSD method are more reliable than those from the other methods. On the other hand, the comparison of the experimental spectra with the DOS spectra at different levels of theory would allow us to evaluate the sensitivity of DOS spectra depending on different density functional calculations. They also indicate that the photoelectron experimental results can act as a benchmark to evaluate the accuracy of the calculations at different levels of theory.

5. Discussion

As shown in Fig. 2, we can see that the most stable isomers of AuGe_n^- with $n = 2-10$ are all exohedral structures with the Au atom capping the vertex, edge, or face of Ge_n clusters. Note that the previous calculations predicted the ground state structure of AuGe_{10}^- to be an endohedral D_{5h} symmetric pentagonal prism with the Au atom at the center.^{30,32} In this work, we found that the global minimum of AuGe_{10}^- is an exohedral structure with the Au atom interacting with a Ge_{10} bicapped tetragonal antiprism (10A) while the D_{5h} symmetric pentagonal prism structure (10C) is higher in energy than 10A by 0.23 eV. At $n = 11$, the most stable structure is an endohedral structure. As for AuGe_{12}^- , the most stable structure is an endohedral I_h symmetric icosahedral structure with the Au atom located at the center and twelve Ge atoms situated at its icosahedral vertices, which is very similar to the structure of the superatom Al_{13}^- investigated in the literature.⁴⁵⁻⁵⁴ Interestingly, our photoelectron

experimental data show that the AuGe_{12}^- cluster has a large VDE of 3.60 eV, which is very close to the EAs of the Cl atom (3.61 eV)⁵⁵ and Al_{13} (3.57 eV).⁴⁹ The I_h symmetric icosahedral structure AuGe_{12}^- may serve as a superhalogen anion, similar to Al_{13}^- in the case of $\text{K}^+\text{Al}_{13}^-$,⁵¹ to form an ionically bonded molecule $\text{K}^+[\text{AuGe}_{12}]^-$, which would then represent potential building blocks for the assembly of novel nanostructured materials.⁵⁰ Our calculations found that the most stable structure of neutral AuGe_{12} is slightly distorted compared to its anionic counterpart, in agreement with the previous theoretical results of AuGe_{12} .²⁹ The structure of the AuGe_{12}^- anion is more symmetric than that of the neutral molecule because the AuGe_{12}^- anion has a closed-shell electronic configuration while the neutral AuGe_{12} is one electron less than that of closed-shell electronic configuration. The Wade-Mingos rules predicted that a *close* icosahedral $\text{TM}@\text{E}_{12}$ structure can be formed for a system with $4n + 2 = 50$ valence electrons, in which $4n = 48$ electrons are coming from the E_{12} cluster and the other two electrons are contributed from the net charge or the $(n + 1)s$ subshell of TM.³³ Here, the I_h icosahedral structure of AuGe_{12}^- exactly obeys the electron counting rules, indicating that it is also stable from the electronic shell perspective.

It is worth mentioning that the previous studies suggested the most stable structure of AuGe_{12}^- to be an endohedral D_{2d} symmetric bicapped pentagonal prism with the Au atom at the center,^{31,32} different from the I_h icosahedral structure in this work. Actually, we have tried the D_{2d} symmetric bicapped pentagonal prism during the geometric structure searching for AuGe_{12}^- , but it is not a local minimum and is relaxed into a less symmetric structure (12D) after optimization. Why the other investigations calculated at the B3LYP/LanL2dz level of theory found the D_{2d} symmetric structure to be the most stable structure? It may be explained by two main aspects. On one hand, it is well known that the LanL2dz basis set is not enough to describe correctly the bonding and the structure of AuGe mixed systems because the LanL2dz basis set does not involve the d orbitals of the Ge atoms, which are very important to describe the bonding for such AuGe mixed systems. On the other hand, the relative energies of AuGe_n^- isomers also depend on the B3LYP/LanL2dz level of theory, which is much less accurate to evaluate the energetic ordering of isomers than the CCSD method. We guess that the hybrid functional can lead to the relativistic radial expansion and energetic destabilization of 5d shells of the Au atom due to the relativistic effect, which may prompt the interactions between its 5d orbitals and the 4s4p hybridized orbitals of Ge_{12} cage, as a result, making the I_h structure to be more stable than the D_{2d} symmetric structure. This may explain why the previous theoretical calculations found that the interactions between the metal 5d orbitals and the Ge_{12} cage are smaller in the icosahedral cage than the D_{2d} symmetric cage.³³ In fact, the molecular orbital analysis proved that the interactions exist between the 5d orbitals of the Au atom and the 4s4p hybridized orbitals of the Ge_{12} cage, which would be described in detail in the following section.

The formation of stable endohedral structures for AuGe_n clusters at $n = 11$ and 12 can be explained partially by the bond strength between the metal dopant and germanium clusters.⁵⁶

Neckel *et al.*⁵⁷ and Shima *et al.*⁵⁸ have reported that the bond strength of Au-Ge (2.84 eV) is stronger than that of Ge-Ge (2.78 eV) and the bond length of Au-Ge (2.46 Å) is similar to that of Ge-Ge (2.44 Å), indicating that the Ge atoms prefer to form a bond with the Au atom rather than interact with some other Ge atoms. In other words, the formation of Au-Ge bonds can contribute to enhanced stability of AuGe_n^- clusters compared to Ge-Ge bonds, which may explain why the I_h symmetric icosahedral structure can form.

To further investigate the chemical bonding properties of the AuGe_{12}^- cluster, the molecular orbital diagrams of the most stable isomer (12A) of AuGe_{12}^- were analyzed and displayed in Fig. 4. The HOMO is mainly composed of the $5d_{xy}$ orbital of the Au atom and the 4s4p hybridized orbitals of the Ge atoms, while the HOMO-1 has the components from the $5d_{x^2-y^2}$ orbital of the Au atom and the 4s4p hybridized orbitals of the Ge atoms. The $5d_{z^2}$ orbital of the Au atom and the 4s4p hybridized orbitals of the Ge atoms are primarily involved in the HOMO-2. The HOMO-3 is mainly constructed by the $5d_{xz}$ orbital of the Au atom and the 4s4p hybridized orbitals of the Ge atoms, while the HOMO-4 consists of the $5d_{yz}$ orbital of the Au atom and the 4s4p hybridized orbitals of the Ge atoms. These molecular orbitals suggest that there are interactions between the 5d orbitals of the Au atom and the 4s4p hybridized orbitals of the Ge atoms. The LUMO+4 to LUMO+8 orbitals of the AuGe_{12}^- cluster were also analyzed and displayed in Fig. 4, which clearly suggest that the Au 5d-Ge 4s/4p antibonding character drifts up into the vacant orbitals. Besides, the Au 5d-Ge 4s/4p bonding character is not found in other vacant orbitals. Therefore, the orbitals of HOMO-HOMO-4 are all doubly occupied and the 5d orbitals of the Au atom are involved in the bonding rather than antibonding. It seems that the delocalized Au-Ge interactions strengthen the Au-Ge bonds, therefore, make the I_h symmetric icosahedral structure of AuGe_{12}^- stable. This is consistent with the conclusion that the formation of Au-Ge bonds can contribute to enhanced stability of AuGe_n^- clusters compared to Ge-Ge bonds. As mentioned above, the relativistic effect can result in the relativistic radial expansion and energetic destabilization of 5d shells of the Au atom, which may prompt the interactions between its 5d orbitals and the 4s4p hybridized orbitals of the Ge_{12} cage. The contribution of 5d orbitals in the HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4 causes an increasing population of electrons on the Au atom, implying that the 5d orbitals may stabilize the Ge_{12} cage and promote the Au atom to be encapsulated in the cage of Ge_{12} , as pointed out by theoretical calculations.⁵⁹ Similarly cooperative stabilization between the metal d orbitals and the sp hybridized cage has been reported in the theoretical investigation of $\text{Zr}@\text{C}_{28}$,⁶⁰ in which the d orbitals of the Zr atom can electronically contribute to encourage the encapsulation in the carbon cage and stabilize the C_{28} cage. Besides, the experimental results of anion photoelectron spectroscopy of germanium clusters containing transition or lanthanide-metal atoms, MGe_{16}^- ($\text{M} = \text{Sc-V}, \text{Y-Nb}, \text{and Lu-Ta}$),⁶¹ also suggested the interactions between the d orbitals of metal and the sp hybridized Ge_{16} cage can promote

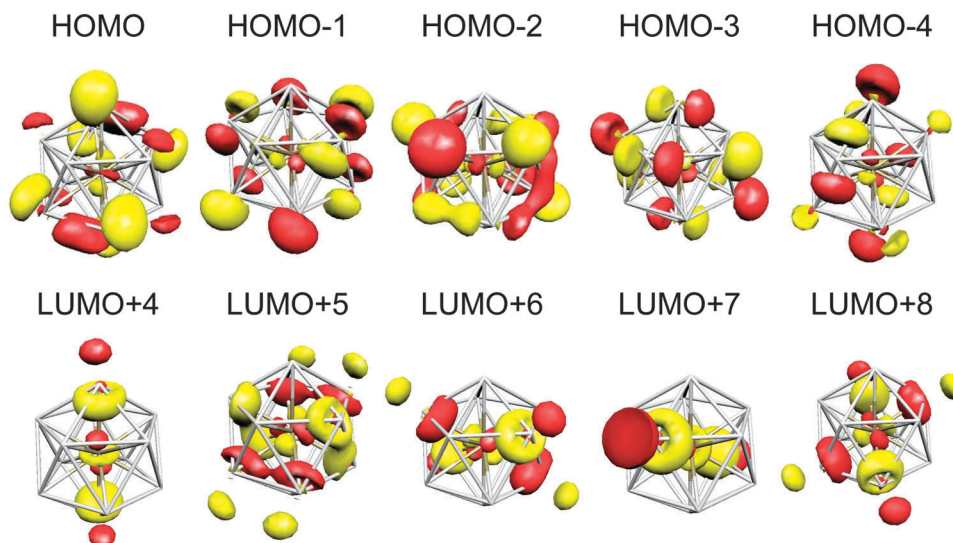


Fig. 4 Molecular orbitals of the I_h symmetric icosahedral AuGe_{12}^- cluster.

encapsulation of the metal and stabilize the spherical structure of the Ge_{16} cage.

Spherical aromaticity arising from electron delocalization is likely another important factor that contributed to the chemical stability of the AuGe_{12}^- cluster. The negative magnetic shielding at the center of the cage equals the nucleus-independent chemical shift (NICS) value,^{62,63} which can be used to assess the degree of aromaticity for various cage structures, for example, $I_h\text{-C}_{60}$ (−2),⁶⁴ $I_h\text{-Au}_{32}$ (−100),⁶⁴ $I_h\text{-Si}_{60}$ (−1.4),⁶⁵ $I_h\text{-Ge}_{60}$ (−1.5),⁶⁵ $T_d\text{-Al}_4\text{Si}_{28}$ (−36),⁶⁶ $T_d\text{-Ga}_4\text{Si}_{28}$ (−45),⁶⁶ and $T_d\text{-In}_4\text{Si}_{28}$ (−52);⁶⁶ in general, the more negative the NICS, the stronger the aromaticity. The original NICS index ($\text{NICS}(0)_{\text{iso}}$) was based on the total isotropic shielding computed at the ring centers, however, $\text{NICS}(0)_{\text{iso}}$ is non-zero for some nonaromatic rings due to some local effects.⁶⁷ Consequently, isotropic $\text{NICS}(1)$ computed at points 1 Å above the ring centers where these local contributions fall off rapidly, was recommended.^{67,68} We calculated the $\text{NICS}(0)$ and $\text{NICS}(1)$ of the icosahedral AuGe_{12}^- cluster at the B3LYP/SDD/Au/6-311+G(d)/Ge level of theory using the GAUSSIAN 09 program package. The $\text{NICS}(0)$ and $\text{NICS}(1)$ values are calculated to be −143.7 ppm and −36.3 ppm, respectively, indicating that the icosahedral AuGe_{12}^- cluster is significantly aromatic. It should be mentioned that the D_{2d} structure of the AuGe_{12}^- cluster has also been reported to be aromatic.³¹

6. Conclusions

The structural evolution and electronic properties of AuGe_n^- ($n = 2\text{--}12$) clusters were investigated by using anion photoelectron spectroscopy in combination with *ab initio* calculations. The most stable structures of AuGe_n^- with $n = 2\text{--}10$ clusters are all exohedral structures, while AuGe_{11}^- is confirmed to be the critical size of the endohedral structure and AuGe_{12}^- is an I_h symmetric icosahedral structure with the Au atom located at the center. The molecular orbital analysis of the AuGe_{12}^- cluster

suggests that the interactions between the 5d orbitals of the Au atom and the 4s4p hybridized orbitals of the Ge atoms may stabilize the I_h symmetric icosahedral cage and promote the Au atom to be encapsulated in the cage of Ge_{12} . The calculated $\text{NICS}(0)$ and $\text{NICS}(1)$ values of the icosahedral AuGe_{12}^- cluster are −143.7 ppm and −36.3 ppm, respectively, indicating that it is significantly aromatic.

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