Research Article

***Ab Initio* Theoretical Investigation on the Geometrical and Electronic Structures of Gallium Aurides: $\text{GaAu}_n^{0/-}$ and $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$)**

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This study presents a systematic investigation of the geometric and electronic properties of $\text{GaAu}_n^{0/-}$ and $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$) clusters based on density functional theory and wave function theory. Detailed orbital analyses, adaptive natural density partitioning, and electron localization function analyses are performed and relevant results are discussed. $\text{GaAu}_n^{0/-}$ ($n = 1-4$) clusters with n -Au terminals and $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$) clusters with bridged Au atoms possess geometric structures and bonding patterns similar to those of the corresponding gallium hydrides $\text{GaH}_n^{0/-}$ and $\text{Ga}_2\text{H}_n^{0/-}$. Ga–Au interaction is predicted to occur through highly polar covalent bonds in monogallium aurides. In contrast to the highly symmetric ground states of C_{2v} Ga_2Au , C_{2v} Ga_2Au_2 , and D_{3h} Ga_2Au_3 , C_{3v} Ga_2Au_4 is composed of strong interactions between a Ga^+ cation and the face of a tetrahedral GaAu_4^- anion. The adiabatic and vertical detachment energies of the anions under study are calculated to facilitate their experimental characterization. Geometric and electronic structural comparisons with the corresponding gallium hydrides are conducted to establish an isolobal analogy between gold and hydrogen atoms.

1. Introduction

Considering its strong relativistic effects, Au is highly different from other coinage metals (Cu and Ag); Au has the highest electron affinity (2.3086 eV) of any element other than the halogens as well as the highest electron negativity (2.4 in the Pauling scale) among all of the metals [1–4]. The H/Au isolobal is an extension of the most remarkable experimental discovery of the H/AuPR₃ analogy thus far and has helped elucidate the structures and bonding types in various ligated Au compounds [5, 6]. The H/Au isolobal relationship in gas-phase Si–Au alloy clusters and B–Au alloy clusters, such as $\text{SiAu}_4^{0/-}$ [7], $\text{Si}_2\text{Au}_x^{0/-}$ ($x = 2, 4$) [8, 9], Si_3Au_3 , $\text{B}_7\text{Au}_2^{0/-}$ [10], $\text{B}_6\text{Au}_n^{0/-}$ ($n = 1-3$) [11], $\text{B}_{10}\text{Au}^{0/-}$ [12], and closo-aurobranes $\text{B}_n\text{Au}_n^{2-}$ ($n = 5-12$) [13], has been confirmed by joint photoelectron spectroscopy (PES) and density functional

theory (DFT) investigations. Various compounds with 2c–2e N–Au and B–Au bonds [14–17], relativistic pseudopotential calculations on XAu_n^{m+} containing Au ligands ($\text{X} = \text{B}, \text{N}, \text{Al}, \text{S}$, $n = 4-6$) [18], and Au-bridged $\text{X} \cdots \text{Au}-\text{Y}$ Lewis acid-base pairs have also been reported [19].

The H/Au analogy has recently motivated our group to analyze the geometric and electronic structures of electron-deficient B–Au and Al–Au alloy small clusters, such as those of $\text{BAu}_n^{0/-}$ ($n = 1-4$) [20], $\text{B}_2\text{Au}_n^{0/-}$ ($n = 1, 3, 5$) [21], $\text{B}_2\text{Au}_2^{0/-/2-}$ [22], $\text{AlAu}_n^{0/-}$ ($n = 2-4$) [23], $\text{Al}_2\text{Au}_n^{0/-}$ ($n = 1-3$) [24], $\text{B}_2\text{Au}_4^{0/-}$, and $\text{Al}_2\text{Au}_4^{0/-}$, based on *ab initio* theories. These studies reveal a clear structural link between electron-deficient Au-containing clusters and the corresponding hydride molecules. Comparative studies on the properties of group IIIA element–Au alloy clusters have also attracted our interest. Boron, aluminum, and gallium

hydrides, as well as their corresponding Au compounds, show several similarities and differences. To the best of our knowledge, no investigations on gallium aurides are yet available.

The present study describes a detailed *ab initio* investigation on the geometric and electronic structures of $\text{GaAu}_n^{0/-}$ and $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$) based on DFT and wave function theory. Natural resonance theory (NRT) and electron localization function (ELF) [25, 26] are performed to characterize Ga–Au bonds in monogallium aurides. Natural localized molecular orbitals (NLMO) and adaptive natural density partitioning (AdNDP) [27] are performed to discuss the chemical bonding in digallium aurides. The adiabatic electron detachment energies (ADEs) and vertical electron detachment energies (VDEs) of GaAu_n^- and Ga_2Au_n^- ($n = 1-4$) anions are calculated to aid their PES characterization. The results obtained in this work extend the concept of bridging Au interactions and enrich the chemistry of Au.

2. Theoretical Methods

Structural optimizations and frequency analyses were conducted on low-lying isomers using the hybrid B3LYP method [28, 29] and the second-order Møller-Plesset approach by frozen core approximation [MP2(FC)] [30, 31]. MP2 produces ground state structures and relative energy orders similar to B3LYP with slightly different bond parameters. Relative energies for the lowest-lying isomers were further refined using the coupled cluster method with triple excitations [CCSD(T)] [32] at B3LYP structures. Stuttgart quasi-relativistic pseudopotentials and basis sets augmented with two f-type polarization functions and one g-type polarization function (Stuttgart_rsc_1997_ecp+2f1g ($\alpha(f) = 0.498$, $\alpha(f) = 1.464$, and $\alpha(g) = 1.218$)) [33] were employed for Au with 19 valence electrons. The augmented Dunning's correlation consistent basis set of aug-cc-pvTZ [34] was used for Ga throughout this work. Bonding analyses were accomplished using NRT, NLMO, AdNDP [27], and ELF [25, 26]. The ADEs and VDEs of the anions were calculated as the energy differences between the anions and the corresponding neutrals at their ground state and anionic structures, respectively. All calculations in this work were performed using Gaussian 09 [35]. AdNDP and ELF analyses were performed with Multiwfn [36]. The NBO5.0 [37] program was used to calculate bond orders and atomic charges.

3. Results and Discussion

3.1. Geometric and Electronic Structures of GaAu_n and GaAu_n^- ($n = 1-4$). $\text{GaAu}_n^{0/-}$ ($n = 1-4$) clusters with n -Au terminals possess geometric structures and bonding patterns similar to those of the corresponding gallium hydrides $\text{GaH}_n^{0/-}$ [38]. As shown in Figure 1, low-spin electronic states are consistently favored in $\text{GaAu}_n^{0/-}$ ($n = 1-4$). At all levels of theory, the ground structure GaAu^- anion (**1**, $^2\Sigma^+$) has a bond length of $r_{\text{Ga-Au}} = 2.52 \text{ \AA}$ and is 1.76 eV more stable than its quartet isomer (**2**, $^4\Sigma^+$) at the CCSD(T) level. The most stable

GaAu neutral structure (**3**, $^1\Sigma^+$) possesses a bond length of $r_{\text{Ga-Au}} = 2.45 \text{ \AA}$. For GaAu_2 , the V-shaped C_{2v} GaAu_2^- (**5**, 1A_1) with a bond length of $r_{\text{Ga-Au}} = 2.55 \text{ \AA}$ is the ground state and is 0.80 eV more stable than the linear $C_{\infty v}$ GaAu_2^- (**6**, $^1\Sigma^+$) at the CCSD(T) level. V-shaped C_{2v} GaAu_2 (**7**, 2B_2) is the most stable geometry on the potential surface of neutral GaAu_2 . A large geometric change may be observed upon electron detachment from the anion C_{2v} GaAu_2^- **4** to the neutral C_{2v} GaAu_2 **7**, although these molecules have the same symmetry: the Ga–Au bond length increases by 0.08 Å, the Au–Au distance decreases by 1.19 Å, and the Au–Ga–Au bond angle considerably decreases by 38° in the anion relative to the neutral molecule.

The perfect planar triangular GaAu_3^- structure has D_{3h} symmetry (**9**, $^2A_1'$) with a bond length of $r_{\text{Ga-Au}} = 2.49 \text{ \AA}$ and an Au–Ga–Au bond angle of $\text{AuGaAu} = 120^\circ$. This structure is the ground state form and is 0.18 eV more stable than the off-plane C_s GaAu_3^- (**10**, $^2A'$) at the CCSD(T) level. Neutral GaAu_3 (**11**, $^1A_1'$) with an sp^2 hybridized Ga at the center of the molecule is a closed-shell singlet with D_{3h} symmetry. Compared with the anion, the neutral molecule only exhibits slight shortening of the Ga–Au bond length (0.1 Å).

On GaAu_4^- , we calculated several isomers and found that the perfect tetrahedral T_d GaAu_4^- (**13**, 1A_1) has an sp^3 hybridized Ga. This structure is the ground geometry; here, the four –Au terminals are singly σ -bound to the central Ga with a bond length of $r_{\text{Ga-Au}} = 2.45 \text{ \AA}$ and a Wiberg bond index of $\text{WBI}_{\text{Ga-Au}} = 0.93$. T_d GaAu_4^- (**13**) is separated by at least 0.14 eV from other 2D and 3D isomers at the CCSD(T) level, which suggests that an Ga^- tetrahedral center is strongly favored in the GaAu_4^- anion. Interestingly, T_d GaAu_4^- (**13**) has the shortest Ga–Au bond length and the largest HOMO-LUMO energy gap of $\Delta E_{\text{gap}} = 2.89 \text{ eV}$ in the GaAu^- series. Detaching one electron from the perfect tetrahedral T_d GaAu_4^- (**13**) involves a John-Teller process to produce the severely distorted global minimum of C_s GaAu_4 (**16**, $^2A'$), which lies at least 0.22 eV higher than those of other low-lying isomers at the CCSD(T) level.

3.2. Bonding Consideration of GaAu_n and GaAu_n^- ($n = 1-4$). NRT was used to calculate the bond orders and bond polarities of the molecules under study. As shown in Table 1, covalent contributions to the Ga–Au interactions continuously increase in the GaAu_n^- series from $n = 1$ to $n = 4$. The Ga–Au bonds in T_d GaAu_4^- (**13**) have the highest percentage of covalence (78%). The Ga–Au bonds in D_{3h} GaAu_3^- (**9**), C_{2v} GaAu_2^- (**5**), and $C_{\infty v}$ GaAu^- (**1**) show covalent contributions of 54%, 44%, and 40%, respectively. This result indicates that Ga–Au interactions in the GaAu_n^- series render the characteristics of ionic structures, especially in GaAu_2^- and GaAu^- . The characteristic of the Ga–Au bond in the GaAu_n^- series is also illustrated clearly by ELF analysis [27], which reflects the probability of finding an electron or a pair of pairs in specific basins (Figure 2). Contour line maps of $C_{\infty v}$ GaAu^- (**1**), C_{2v} GaAu_2^- (**5**), D_{3h} GaAu_3^- (**9**), and T_d GaAu_4^- (**13**) reveal the presence of a weak electronic interaction between Ga and Au. This interaction is a highly polar covalent bond. NBO quantitatively reveals

FIGURE 1: Low-lying isomers of (a) GaAu^- , (b) GaAu , (c) GaAu_2^- , (d) GaAu_2 , (e) GaAu_3^- , (f) GaAu_3 , (g) GaAu_4^- , and (h) GaAu_4 at the B3LYP level. Relative energies ΔE (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP are also indicated (bond lengths in angstrom and bond angles in degree).

TABLE 1: Full valency, covalency, and electrovalency indices, covalent percentages, and natural atomic charges ($q/|e|$) calculated for GaAu_n^- anions.

Isomers	Atom	Valency	Covalency	Electrovalency	Covalent percentage	q
1 $C_{\infty v}$ GaAu^-	Ga	1.02	0.41	0.61	0.40	-0.44
	Au	1.02	0.41	0.61	0.40	-0.56
5 C_{2v} GaAu_2^-	Ga	2.03	0.87	1.15	0.43	0.05
	Au	1.01	0.44	0.58	0.44	-0.53
9 D_{3h} GaAu_3^-	Ga	2.85	1.53	1.32	0.54	0.08
	Au	0.96	0.51	0.45	0.53	-0.36
11 T_d GaAu_4^-	Ga	3.77	2.95	0.82	0.78	-0.34
	Au	0.94	0.74	0.20	0.79	-0.17

the Ga–Au bonding properties: the Ga–Au bond length of $r_{\text{Ga–Au}} = 2.45\text{--}2.55 \text{ \AA}$ and the corresponding bond order of $\text{WBI}_{\text{Ga–Au}} = 0.73\text{--}0.90$ in the GaAu_n^- series. These properties further indicate that the interaction is covalent but with ionic characteristics.

In the GaAu_n^- series, the perfect tetrahedral T_d GaAu_4^- (13) is unique. Figure 3 shows the four valence molecular orbitals of the molecule, including a triply degenerate HOMO

(t_2) and a singlet HOMO-1 (a_1). T_d GaAu_4^- has a bonding pattern similar to that of T_d GaH_4^- , with an sp^3 hybridized Ga center surrounded by four Au atoms to form four equivalent σ single bonds. The B–Au and B–H σ bonds in T_d GaAu_4^- and T_d GaH_4^- show subtle differences in orbital composition because of obvious relative effects in Au. T_d GaAu_4^- possesses the orbital combination of $\text{MO}_{\text{Ga–Au}} = 0.63(sp^3)_{\text{Ga}} + 0.77(sd^{0.05})_{\text{Au}}$ and the corresponding atomic

FIGURE 2: Contour line maps of electron localization functions (ELFs) in GaAu⁻ (1), GaAu₂⁻ (5), GaAu₃⁻ (9), and GaAu₄⁻ (13).

FIGURE 3: Comparison of the four valence MOs responsible for the four equivalent σ -bonds in T_d [GaAu₄]⁻ and T_d [GaH₄]⁻ at the B3LYP level.

contribution of 40%Ga + 60%Au, with Au 6s contributing 95.2% and Au 5d contributing 4.7% to the Au-based orbital. In GaAu_n⁻ ($n = 1-4$), Au 5d contributes 8.5%–4.7% to the Au-based orbital, which is less than that in monoboron aurides.

3.3. Geometric and Electronic Structures of Ga₂Au_n and Ga₂Au_n⁻ ($n = 1-4$). All low-lying neutral and anion clusters of Ga₂Au_n^{0/-} ($n = 1-4$) are summarized in Figure 4. Ga₂Au_n^{0/-} ($n = 1-4$) clusters with bridged Au atoms possess geometric structures similar to those of the corresponding gallium hydrides Ga₂H_n^{0/-} [38]. As shown in Figures 4(a) and 4(b), the smallest digallium auride Ga₂Au^{0/-} contains a bridging Au atom. Anionic Ga₂Au⁻ exhibits three possible structures: triplet Au-bridged V-shaped (C_{2v} , **18**, 3B_1), singlet

Au-bridged V-shaped (C_{2v} , **19**, 1A_1), and triplet linear ($C_{\infty v}$, **20**, $^3\Sigma_g^-$). At the CCSD(T) level, the triplet Au-bridged structure **18** with bond lengths of $r_{\text{Ga-Au}} = 2.62 \text{ \AA}$ and $r_{\text{Ga-Ga}} = 2.67 \text{ \AA}$, respectively, lies 0.22 and 0.47 eV lower than the singlet Au-bridged **19** and triplet linear **20** structures. This result suggests that the triplet Au-bridged C_{2v} Ga₂Au⁻ (3B_1 , **18**) is the ground state of Ga₂Au⁻. Similar to the V-shaped Ga₂H (Ga(μ -H)Ga), the doublet Au-bridged C_{2v} Ga₂Au (**21**, 2B_1) is a global minimum lying 0.72 eV lower than the linear $C_{\infty v}$ Ga₂Au (**22**) at the CCSD(T) level. Adding one Au atom to bridge two Ga atoms in C_{2v} Ga₂Au⁻ (**18**) and C_{2v} Ga₂Au (**21**), respectively, produces the ground states of the off-plane di-Au-bridged C_{2v} Ga₂Au⁻ ([Ga(μ -Au)₂Ga]⁻) (**23**, 2A_1) and C_{2v} Ga₂Au₂ ([Ga(μ -Au)₂Ga]) (**26**, 1A_1), which are at least 0.43 and 0.67 eV, respectively, more stable than other isomers. Di-Au-bridged C_{2v} Ga₂Au₂ (**26**)

FIGURE 4: Low-lying isomers of (a) Ga₂Au⁻, (b) Ga₂Au, (c) Ga₂Au₂⁻, (d) Ga₂Au₂, (e) Ga₂Au₃⁻, (f) Ga₂Au₃, (g) Ga₂Au₄⁻, and (h) Ga₂Au₄ at the B3LYP level. Relative energies ΔE (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP are also indicated (bond lengths in angstrom).

possesses the same geometry as di-H-bridged C_{2v} Ga_2H_2 . For $X_2Au_2^{0/-}$ ($X=B, Al, Ga$) systems, the global minima of $Ga_2Au_2^{0/-}$ and $Al_2Au_2^{0/-}$ show similar V-shaped geometries. Both molecules differ from $B_2Au_2^{0/-}$, which favors a linear structure containing a multiple-bonded BB core terminated by two Au atoms. This finding further demonstrates the presence of a strong chemical interaction between two B atoms in diboron aurides.

The interaction between two Ga atoms is so weak that two Au atoms prefer to bond with digallium auride isomers, such as $D_{\infty h}$ Ga_2Au_2 (28). The anion $Ga_2Au_3^-$ prefers a tri-Au-bridged $[Ga(\mu-Au)_3Ga]^-$ form with a singlet electronic structure. The most stable geometry of the tri-Au-bridged D_{3h} $Ga_2Au_3^-$ (29, $^1A'_1$) with a bond length of $r_{Ga-Au} = 2.69 \text{ \AA}$ is at least 0.37 and 0.02 eV more stable than di-Au-bridged C_s $Ga_2Au_3^-$ (30, $^1A'$) at the MP2 and CCSD(T) levels, respectively. Similar to Ga_2H_3 favoring a tri-H-bridged $[Ga(\mu-H)_3Ga]$ structure, the global minimum of Ga_2Au_3 is the tri-Au-bridged D_{3h} Ga_2Au_3 ($^2A'_1$, 32), which lies 0.54 and 1.17 eV lower than di-Au-bridged C_s $Ga_2Au_3^-$ (33, $^2A'$) and planar C_{2v} $Ga_2Au_3^-$ (34, 2A_1), respectively. The Ga–Ga distance decreases by 0.48 Å and the Ga–Au bond length decreases by 0.09 Å in anion 29 relative to the neutral molecule 32. This result indicates a large geometry change upon electron detachment from the anion to the neutral molecule, although they have the same symmetry.

Adding one Au atom terminally to a Ga in D_{3h} $Ga_2Au_3^-$ $[Ga(\mu-Au)_3Ga]^-$ (29, $^1A'_1$) produces the ground state of tri-Au-bridged C_{3v} $Ga_2Au_4^-$ $[Ga(\mu-Au)_3Ga]Ga^-$ (35, 2A_1), which is 0.44, 1.33, and 0.92 eV more stable than di-Au-bridged C_{2v} $Ga_2Au_4^-$ (36, 2A_1), distorted Y-shaped C_s $Ga_2Au_4^-$ (37, $^2A'$), and mono-Au-bridged C_1 $Ga_2Au_4^-$ (38, 2A) at the CCSD(T) level, respectively. Ga_2Au_4 has the same high-symmetry ground state of tri-Au-bridged C_{3v} Ga_2Au_4 $Au^+[Ga(\mu-Au)_3Ga]^-$ (39, 1A_1), which lies 1.61, 1.22, and 1.57 eV lower than Y-shaped C_s Ga_2Au_4 (40, $^1A'$), mono-Au-bridged Ga_2Au_4 (41, $^1A'$), and nonbridged perpendicular D_{2d} Ga_2Au_4 (42, 1A_1), respectively. Similar to the tri-H-bridged C_{3v} Ga_2H_4 [39], tri-Au-bridged C_{3v} Ga_2Au_4 (39) is composed of strong interactions between a Ga^+ cation and the face of a tetrahedral $GaAu_4^-$ anion. The global minima of Ga_2Au_4 and Al_2Au_4 have the same ionic conformer; both molecules differ from B_2Au_4 , which has a di-Au-bridged covalent structure.

3.4. Bonding Consideration of Ga_2Au_n and $Ga_2Au_n^-$ ($n = 1-4$). AdNDP analysis [27] is an effective tool for analyzing the bonding patterns of various organic and inorganic molecules. As shown in Figure 5, other bonds besides the lone pairs of the Au atom may be analyzed as follows. C_{2v} Ga_2Au (21) contains one localized Ga–Ga 2c–2e σ -bond with an occupation number of ON = 1.96 |e|, one localized Ga–Ga 2c–2e σ -anti-bond with an occupation number of ON = 1.96 |e|, and one delocalized Ga–Au–Ga 3c–2e bond with an occupation number of ON = 2.00 |e|. C_{2v} Ga_2Au_2 (26) contains one localized Ga–Ga 2c–2e σ -bond with an occupation number of ON = 1.90 |e|, one localized Ga–Ga 2c–2e σ -anti-bond with

an occupation number of ON = 1.90 |e|, and two delocalized Ga–Au–Ga 3c–2e bonds with an occupation number of ON = 1.97 |e|. D_{3h} Ga_2Au_3 (32) contains three delocalized Ga–Au–Ga 3c–2e bonds with an occupation number of ON = 1.94 |e|. C_{3v} Ga_2Au_4 (39) contains one localized $Ga_{(2)}-Au_{(t)}$ 2c–2e σ -bond with an occupation number of ON = 1.95 |e| and three delocalized Ga–Au–Ga 3c–2e bonds with an occupation number of ON = 1.93 |e|. The same number of electrons occupies the bonding and antibonding orbitals in C_{2v} Ga_2Au (21) and C_{2v} Ga_2Au_2 (26). Thus, no electronic effect is produced between two Ga atoms and the delocalized Ga–Au–Ga 3c–2e bond is the main interaction in high symmetric Ga_2Au_n ($n = 1-4$).

Detailed NLMO analyses quantitatively reveal the existence of bridging Ga–Au–Ga 3c–2e bonds in C_{2v} Ga_2Au (21), C_{2v} Ga_2Au_2 (26), D_{3h} Ga_2Au_3 (32), and C_{3v} Ga_2Au_4 (39), as clearly shown in an image of their 3c–2e orbital and orbital combination (Figure 6). In C_{2v} Ga_2Au (21), the 3c–2e bond possesses the orbital combination of $\tau_{Ga-Au-Ga} = 0.38(sp^{99.9})_{Ga} + 0.83(sd^{0.02})_{Au} + 0.38(sp^{99.9})_{Ga}$ and the corresponding atomic contribution of 15%Ga + 70%Au + 15%Ga. In the Ga–Au–Ga 3c–2e bond, Au 6s contributes 97.8% and Au 5d contributes 1.64% to the Au-based orbital, whereas Ga 4p contributes 98.2% and Ga 4s contributes 0.76% to the Ga-based orbital. Obviously, Au 6s and Ga 4p provide the largest contributions to the Ga–Au–Ga 3c–2e bond, and it can be practically approximated as $\tau_{Ga-Au-Ga} = 0.38(p)_{Ga} + 0.83(sd^{0.02})_{Au} + 0.38(p)_{Ga}$. The orbital combinations of Ga–Au–Ga 3c–2e bond in C_{2v} Ga_2Au_2 (26) [$\tau_{Ga-Au-Ga} = 0.39(p)_{Ga} + 0.83(sd^{0.01})_{Au} + 0.39(p)_{Ga}$] and D_{3h} Ga_2Au_3 (32) [$\tau_{Ga-Au-Ga} = 0.42(p)_{Ga} + 0.80(sd^{0.02})_{Au} + 0.42(p)_{Ga}$] are surprisingly similar to that of C_{2v} Ga_2Au (21). However, the composition of the 3c–2e orbital in C_{3v} Ga_2Au_4 (39) is obviously different from that in Ga_2Au_n ($n = 1-3$). Each 3c–2e bond has an orbital combination of $\tau_{Ga(1)-Au-Ga(2)} = 0.40(sp^{99.9})_{Ga(1)} + 0.70(sd^{0.02})_{Au} + 0.59(sp^{4.73})_{Ga(2)}$ and the corresponding atomic contribution of 16%Ga₍₁₎ + 50%Au + 35%Ga₍₂₎.

In the bridging $Ga_{(1)}-Au-Ga_{(2)}$ 3c–2e bond, bridged Au 6s and 5d, respectively, contribute 80.7% and 1.4% to the Au-based orbital, $Ga_{(1)}$ 4s and 4p, respectively, contribute 0.7% and 98.6% to the $Ga_{(1)}$ -based orbital, and $Ga_{(2)}$ 4s and 4p, respectively, contribute 17.3% and 81.8% to the $Ga_{(2)}$ -based orbital. Obviously, the 17.3% contribution from $Ga_{(2)}$ is not negligible because of the $Ga_{(2)}$ atom of the $GaAu_4^-$ unit. Au 6s and $Ga_{(1)}$ 4p provide the largest contributions to the $Ga_{(1)}-Au-Ga_{(2)}$ bridging bond in C_{3v} Ga_2Au_4 (39). This finding agrees with the ionic characteristic of $Au_{(t)}^+[Ga_{(1)}(\mu-Au)_3Ga_{(2)}]^-$ presented earlier. Thus, in contrast to the orbital combination in Ga_2Au_n ($n = 1-3$), the bridging bond of C_{3v} Ga_2Au_4 (39) can be approximated as $\tau_{Ga(1)-Au-Ga(2)} = 0.40(p)_{Ga(1)} + 0.70(sd^{0.02})_{Au} + 0.59(sp^{4.73})_{Ga(2)}$. Similar 3c–2e orbital combinations exist in the corresponding anions. Compared with the bridging Au 3c–2e bond observed in electron-deficient systems (B_2Au_n , Al_2Au_n , and Ga_2Au_n), we found that bridging Au provides greater contributions to dialuminum and digallium aurides (70%–68%) than to

FIGURE 5: AdNDP bonding patterns of Ga_2Au (21), Ga_2Au_2 (26), Ga_2Au_3 (32), and Ga_2Au_4 (39). Occupation numbers (ON) are also indicated.

TABLE 2: Calculated ADEs (eVs) and VDEs (eV) of digallium auride anions at the B3LYP and CCSD(T)//B3LYP levels. The ADEs of the anions are equivalent to the electron affinities of the corresponding neutrals.

	ADE		VDE	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)
1 $C_{\infty v}$ $GaAu^- (^2\Sigma^+)$	0.64 ($^1\Sigma^+$)	0.30 ($^1\Sigma^+$)	0.66 ($^1\Sigma^+$)	0.60 ($^1\Sigma^+$)
5 C_{2v} $GaAu_2^- (^1A_1)$	2.51 (2B_2)	2.33 (2B_2)	2.75 (2B_2)	2.72 (2B_2)
9 D_{3h} $GaAu_3^- (^2A_1')$	1.99 ($^1A_1'$)	1.56 ($^1A_1'$)	2.10 ($^1A_1'$)	1.86 ($^1A_1'$)
13 T_d $GaAu_4^- (^1A_1)$	3.23 ($^2A_1'$)	3.07 (2T_2)	3.95 ($^2A_1'$)	4.17 (2T_2)
18 C_{2v} $Ga_2Au^- (^3B_1)$	1.47 (2B_1)	1.47 (2B_1)	1.49 (2B_1)	1.50 (2B_1)
23 C_{2v} $Ga_2Au_2^- (^2A_1)$	1.45 (1A_1)	1.46 (1A_1)	1.50 (1A_1)	1.52 (1A_1)
29 D_{3h} $Ga_2Au_3^- (^1A_1')$	2.39 ($^2A_1'$)	2.13 ($^2A_1'$)	2.67 ($^2A_1'$)	2.60 ($^2A_1'$)
35 C_{3v} $Ga_2Au_4^- (^2A_1)$	1.96 (1A_1)	1.55 (1A_1)	2.06 (1A_1)	1.87 (1A_1)

diboron aurides (50%–45%). Specifically, Au 5d contributes less than 2% to the Au-based orbital in dialuminum and digallium aurides.

3.5. Electron Detachment Energies. The ADE and VDE values of the anions were calculated in PES experiments. As shown in Table 2, the B3LYP and CCSD(T)//B3LYP levels produced

consistent one-electron detachment energies for $GaAu_n^-$ and $Ga_2Au_n^-$ ($n = 1-4$) anions. Except for C_{2v} $GaAu_2^-$ (5) and T_d $GaAu_4^-$ (13), D_{3h} $Ga_2Au_3^-$ (29), the calculated ADEs and VDEs at the CCSD(T) level lay at 0.30–1.87 eV. The small differences between ADE and VDE (0.03–0.32 eV) agree with the minor structural relaxation observed between the anion and the corresponding neutral molecule. At the same level,

FIGURE 6: Isosurface maps and orbital combinations of 3c-2e bonds in Ga_2Au^- (18), Ga_2Au (21), Ga_2Au_2^- (23), Ga_2Au_2 (26), Ga_2Au_3^- (29), Ga_2Au_3 (32), Ga_2Au_4^- (35), and Ga_2Au_4 (39).

$C_{2v} \text{ GaAu}_2^-$ (5) shows ADE = 2.33 eV and VDE = 2.72 eV. The difference between the ADE and VDE (0.39 eV) shows considerable structure relaxation between the C_{2v} anion (5) and the C_{2v} neutral molecule (7). A similar result was observed in $D_{3h} \text{ Ga}_2\text{Au}_3^-$ (29). $T_d \text{ GaAu}_4^-$ (13) anion has the calculated one-electron detachment energies of ADE = 3.07 eV and VDE = 4.17 eV at the CCSD(T)//B3LYP level. B3LYP approaches produced close ADE and VDE values with

CCSD(T). The extremely high electron detachment energies of $T_d \text{ GaAu}_4^-$ indicate that GaAu_4 neutrals lie considerably higher than GaAu_4^- anions in energy, while the big ADE-VDE differences (0.72–1.10 eV) agree with the considerable structural relaxation from $T_d \text{ GaAu}_4^-$ (13) and its closely related $C_s \text{ GaAu}_4$ (16). The electron binding energies of these anions fall within the energy range of the conventional excitation laser (266 nm, 4.661 eV) in PES measurements.

4. Summary

This study presents geometric and electronic structural analyses of $\text{GaAu}_n^{0/-}$ and $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$) clusters based on DFT and wave function theory. The structure and bonding of a series of $\text{GaAu}_n^{0/-}$ ($n = 1-4$) with one Ga atom at the center are characterized. NRT, ELF, and NBO analyses show that Ga–Au interactions in the aurogalliums are highly polar covalent bonds with ionic characteristics. $\text{Ga}_2\text{Au}_n^{0/-}$ ($n = 1-4$) is predicted to possess highly symmetric ground states of C_{2v} $\text{Ga}_2\text{Au}_n^{0/-}$, C_{2v} $\text{Ga}_2\text{Au}_2^{0/-}$, D_{3h} $\text{Ga}_2\text{Au}_3^{0/-}$, and C_{3v} $\text{Ga}_2\text{Au}_4^{0/-}$. C_{3v} Ga_2Au_4 present strong interactions between a Ga^+ cation and the face of a tetrahedral GaAu_4^- anion. AdNDP and NLMO analyses demonstrate that a Ga–Au–Ga 3c–2e bond exists in these global minima. Detailed orbital analyses indicate that Au 6s and Ga 4p principally contribute to the Ga–Au–Ga bond in the Ga_2Au_n ($n = 1-3$) complex. In $\text{Ga}^+(\text{GaAu}_4)^-$ ionic conformers, besides Au 6s and cationic Ga 4p, tetrahedral Ga 4s and 4p also contribute significantly to the Ga–Au–Ga bond in Ga_2Au_4 ; here, the tetracoordinate unit has a greater influence than the cationic unit on the total 3c–2e orbital atomic contribution. The predicted ADE and VDE values of GaAu_n^- and Ga_2Au_n^- ($n = 1-4$) may facilitate future PES experiments to confirm these species. Bridging Au interactions addressed in this work provide an interesting bonding mode for covalent and ionic deficient systems and will help design new materials and catalysis with highly dispersed Au atoms.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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