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REGULAR ARTICLE

Structure and stability of $AuXe_n^Z$ ($n = 1$–3, $Z = -1, 0, +1$) clusters

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Abstract We have explored the structures and stabilities of $AuXe_n^Z$ ($n = 1$–3, $Z = -1, 0, +1$) cluster series at CCSD(T) theoretical level. The electron affinities and ionization potentials are correlated to the HOMO–LUMO gaps. The role of the interaction was investigated using the natural bond orbital analysis.

Keywords $AuXe_n^Z$ ($n = 1$–3, $Z = -1, 0, +1$) clusters · Geometrical structure and stability · NBO analysis

1 Introduction

It was always considered that chemical compounds containing rare gas elements could not be formed until the first rare-gas compound, xenon hexafluo-roplatinate [$Xe^+(PtF_6)^-$], was reported four decades ago [1]. The existence of this kind of novel compound with rare gas elements is of considerable significance to open up the new fascinating field in the physics and chemistry. Gold is, in fact generally, regarded as the element whose chemistry is most affected by relativistic effects [2, 3]. This metal is nowadays used in several high-technology fields, like microelectronics and nano-structured material science [4]. It is also very important in catalysis [5–7] and, in this connection, relevant developments concern the catalytic exploitation of Au(I) compounds, which display unique properties governed by relativistic effects [8]. Much studied, as the simplest prototypes for the unconventional reactivity of gold, and in particular of Au(I). Consequently, they are gradually discovered and well investigated in experiment and theory. What has attracted our interest is the Rg–M bonding in the rare gas–noble metal halides, RgMX (Rg = Ar, Kr, Xe; M = Cu, Ag, Au; and X = F, Cl, Br), recently examined with a high-resolution Fourier transform microwave spectrometer [9–21]. Recently, Seidel [22] demonstrated the existence of the $[AuXe_4]^{2+}$ cation in crystal structure of the $AuXe_4{}^{2+}(Sb_2F_{11}^{-1})_2$ compound. The work is very important because it supports the concept that the rare gas atoms can be directly bonded to the gold atom. In these species, the presence of chemical bonds between gold and xenon is in sharp contrast to the conventional behavior of rare gas and noble metal atoms, which are considered to be inert from the existing chemical intuitions. Pyykkö suggested that most of the bonding interaction is covalent in character [23, 24]; the interpretation was questioned by saying that “covalency within the $RgAu^+$ species appears to be unproven” [25], recent investigations showed that there is clearly covalent component in the bonding of $Xe–Au^+$ [26, 27]. However, few investigations have been focused on the interactions of the larger $AuXe_n^+$ clusters and its neutrals and anions, thus the theoretical investigations on this kind of systems and the understanding of their interactions still leave much room for improvement.

In the present study, the investigations of the $AuXe_n^Z$ ($n = 1$–3, $Z = -1, 0, +1$) clusters were performed not only to understand the structure of the systems under consideration, but also to give an insight into the nature of the interaction between Au and Xe atoms. It would be meaningful and interesting to give a description of structures and stability of this new class of compounds.

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2 Computational details

The relativistic pseudo-potentials and the corresponding basis set SDD (6*s*6*p*3*d*1*f*)/[4*s*4*p*3*d*1*f*],are used to describe Xe atom [28]. One set each of diffuse *s*, *p*, and *d* functions (exponents: 0.03, 0.02, 0.05) was added, the single *f* function was replaced by three *f* primitives (1.375, 0.55, 0.22), and one *g* function (0.55) was added, to yield an overall basis set of (7*s*7*p*4*d*3*f*1*g*)/[5*s*5*p*4*d*3*f*1*g*] size [29]. The interactions in rare gas atoms containing compounds often require the inclusion of very high angular momentum functions for accurate description, the present high momentum basis set is proved to be sufficiently accurate and necessary to describe the interaction in our previous works [30, 31].

The 19-valence electron relativistic pseudo-potentials and the ((8*s*7*p*6*d*)/[6*s*5*p*3*d*]) basis set of Dolg are employed for Au atom [32]. Pyykkö found that two *f*-type polarization functions are desirable for the correct description of the interaction energy and the inclusion of an additional *g* function on Au has a sizable effect on the computed bond energy and also leads to a significant shrinking of equilibrium distance, therefore, two *f* functions (0.20 and 1.19) [33] and one *g* function (1.1077) [33] are augmented to describe metallophilic attraction, to yield an overall basis set of (8*s*7*p*6*d*2*f*1*g*)/[6*s*5*p*3*d*2*f*1*g*] size.

The basis set superposition error (BSSE) is corrected by using counterpoise procedure of Boys and Bernardi [34]. The calculations were performed with the Gaussian 03W program [35].

To understand the nature of the interactions, the natural bond orbital (NBO) analysis was used [36, 37]. It provides a simple description of the chemical bond based on orbital interaction concepts. The NBO's are a set of localized orbits that fulfill the requirements of orthonormality and maximum occupancy on the grounds of the calculated MO's after diagonalizing the corresponding electron density matrices. The ab initio wavefunctions transformed to the NBO form are in good agreement with the Lewis model of electronic structure concepts. The transformation to NBO produces both highly occupied and near to empty localized orbits. Consequently, they can be classified as lone pairs (LP), bonding (BD) (corresponding to the Lewis structure). The orbits with smaller occupations are considered as antibonding LP*, BD*, Rydberg (RY), which can be used to describe effects of charge transfer. The energetic stabilization due to $a \rightarrow b$ donor–acceptor interactions can be estimated by second order perturbation theory. In this work, the NBO analysis was performed with the NBO program as implemented in Gaussian 03W program [35].

3 Results and discussion

3.1 Structure

The optimized equilibrium distances, dipole moments, natural population for titled clusters calculated at CCSD(T) theoretical level are given in Table 1. For AuXe^+, the present bond length, 262.8 pm, is in good agreement with Belpassi's result of 260.9 pm [26] and Breckenridge's results of 259.8 pm [27]. For $n = 2$, a linear geometry is optimized for the cation while the bent structures with C_{2v} symmetry were located for the anion and neutral. For $n = 3$, all three-dimensional initial geometries, after the geometry optimization end up planar structures with C_{2v} symmetry for cation and tetrahedron with C_{3v} symmetry for anion and neutral. We noticed that, for $n = 1$ system, the equilibrium Au–Xe distance order is cation < neutral < anion. The distances greatly decrease upon the electron removal. For $n = 2$, upon the electron removal, the distances decrease while the bond angle $\Theta_{\mathrm{Xe-Au-Xe}}$ increase. The anions have loose structures compared to its neutrals and cations.

The Au atom is found to be located inside the Xe atoms, and all the Xe atoms are in the equivalent position except for the $\mathrm{AuXe_3}^+$, and the Xe atoms in $\mathrm{AuXe_3}^+$ are denoted as $\mathrm{Xe_{top}}$, $\mathrm{Xe}_{\mathrm{bot}\text{-}①}$ and $\mathrm{Xe}_{\mathrm{bot}\text{-}②}$, in other systems they are denoted as Xe_i (i = ①–③).

3.2 Stability

The dissociation energies, fragmentation energy, ionization potential (IP), electron affinity (EA), energy gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) is considered to be important parameters in terms of the chemical stability of clusters. The dissociation energies are referenced to the separated-atom limit consisting of ground-state Xe atom(s) and Au^Z ($Z = -1, 0, 1$) ground states. The calculated results at CCSD(T) theoretical level were collected in Table 2.

3.2.1 *Dissociation energy*

For AuXe^+, the present result, 1.1040 eV, is greater than 0.910 eV reported in 1995 by Pyykkö [23] and smaller than that of Belpassi's result of 1.327 eV reported in 2008, the stability error may be resulted by the difference of the methods (relativistic pseudo-potentials and full 4-component Dirac–Coulomb Hamiltonian) and basis sets [26]. For AuXe^- anion, the present results picture an enhanced stability (0.1240 eV) than Pyykkö's results of 0.073 eV at MP2 level and 0.048 eV at CCSD(T) level [23]. The CCSD(T) dissociation energy of 0.0290 eV indicates that

Table 1 The optimized equilibrium distances (*R*/pm, Θ/degree), dipole moments (*D*), natural population analysis calculated at CCSD(T) level

Size	Structure	Natural population analysis	
$n = 1$			
Anion	$R_{Au–Xe} = 368.7$	−0.99644(Au)	−0.00356(Xe)
Neutral	$R_{Au–Xe} = 313.8$	−0.01875(Au)	0.01875(Xe)
Cation	$R_{Au–Xe} = 262.8$	0.85163(Au)	0.14837(Xe)
$n = 2$			
Anion (C_{2v})	$R_{Au–Xe} = 369.0$	−0.99455(Au)	−0.00273(Xe)
	$\Theta_{Xe–Au–Xe} = 70.7$		
Neutral (C_{2v})	$R_{Au–Xe} = 322.5$	−0.02906(Au)	0.001454(Xe)
	$\Theta_{Xe–Au–Xe} = 85.2$		
Cation ($D_{\infty h}$)	$R_{Au–Xe} = 262.2$	0.59791(Au)	0.201050(Xe)
	$\Theta_{Xe–Au–Xe} = 180.0$		
$n = 3$			
Anion (C_{3v}) (Tetrahedron)	$R_{Au–Xe} = 369.5$	−0.98659(Au)	−0.00447(Xe)
	$R_{Xe–Xe} = 424.1$		
	$\Theta_{Xe–Au–Xe} = 70.8$		
Neutral (C_{3v}) (Tetrahedron)	$R_{Au–Xe} = 327.1$	−0.03766(Au)	0.01255(Xe)
	$R_{Xe–Xe} = 430.6$		
	$\Theta_{Xe–Au–Xe} = 82.3$		
Cation (C_{2v}) (Planar)	$R_{Au–Xe(top)} = 283.7$	0.60588(Au)	0.09106(Xe_{top})
	$R_{Au–Xe(bot)} = 265.5$	0.15153(Xe_{bot})	0.15153(Xe_{bot})
	$R_{Xe(bot)–Xe(bot)} = 502.7$		
	$R_{Xe(bot)–Xe(top)} = 467.1$		
	$\Theta_{Xe(bot)–Au–Xe(bot)} = 142.4$		

Table 2 The calculated dissociation energy, HOMO–LUMO gap, ionization potential and electron affinity at CCSD(T) level (energy in eV)

	Anion		Neutral		Cation		Ionization potential	Electron affinity
	D_e	Gap	D_e	Gap	D_e	Gap		
Au ($n = 0$)		5.6768		8.9857		13.3801	9.1767	−2.1609
$n = 1$	0.1240	4.1127	0.0290	8.1142	1.1040	11.8587	7.9047	−2.1779
$n = 2$	0.2754	4.0344	0.0978	7.8015	2.2600	13.1559	6.5139	−2.2128
$n = 3$	0.4492	3.9884	0.1151	7.5816	2.8762	12.1366	6.3539	−2.2520

the neutral system is only very weakly bound at the correlated level.

For $AuXe_2^+$, we arrive the bond length of 262.2 pm and the dissociation energy of 2.260 eV, which are in excellent line with the reported value of 266.0 pm and 2.250 eV, respectively [23]. The present vibrational frequencies of $AuXe_2^+$ are 43.3 (π_u), 119.1 (σ_g), and 259.9 (σ_u) cm^{-1} match Pyykkö's results of 35(π_u), 120 (σ_g) and 182 cm^{-1} (σ_u) [23], whereas for the anion and neutral, the bent structure with C_{2v} symmetry were found, and the stabilities are greatly reduced.

In most electronic spherically symmetric systems, the geometry with high symmetry is preferred; for $AuXe_3^+$, the present results show that the planar D_{3h} geometry with a relative energy of 0.74 meV, while the planar C_{2v} structure with dissociation energy of 2.8762 eV is located.

In cluster physics, the dissociation energy ($D_e(n)$), and the fragmentation energy ($F_e(n) = D_e(n)–D_e(n−1)$) are sensitive quantities that reflect the relative stability of the investigated clusters. More and more Au–Xe "bond" formed with the increase of the cluster size *n* and it results the increase of dissociation energies, which means that these clusters can continuously gain energy during the growth process. The $F_e(2)$ and $F_e(3)$ are 0.1514, 0.1738 for the anion, 0.0688, 0.0173 for the neutral, 1.1560, 0.6162 eV for the cation, respectively. The Au is found to be located inside the Xe atoms, thus the Au–Xe "bonds" increase monotonically as the size of *n* increase while the

Xe–Xe “bond” does not have the same behavior; it results in the monotonically increase of dissociation energies and irregular variable trend of the fragmentation energies.

3.2.2 *Energy gap, ionization potential and electron affinity*

The HOMO–LUMO energy gaps of the Au^+ (13.3801 eV) and Xe (13.6370 eV), are comparable, while those of its anion (Au^-) and neutral (Au) systems are greatly decreased. From Table 2, we can see that the energy gaps decrease monotonically as cluster size n increase for the anion and neutral systems. For the cation systems, the calculated gap of the larger cluster ($AuXe_4{}^+$) is 12.5580 eV, and from Table 2, we can see that the gaps of $n = 0$, 2 and 4 are larger than that of $n = 1$ and 3; furthermore, for the odd-number clusters, the energy gaps increase with cluster size, while they decrease for the even-number clusters, it is expected that the energy gaps converge with the increase of the cluster size n.

The calculated ionization potential of Au, 9.1767 eV, is in agreement with the experimental value of 9.225 eV [38]. The IPs decrease while EAs increase with the cluster size. The geometry structure modifies its geometry upon electron addition or removal in its quest to delocalize the density and Table 1 assist in seeing the structural difference. For $n = 3$ systems, the structure (neutral) is tetrahedron (C_{3v}) and upon charge addition it is slightly distorted from this configuration, it becomes planar C_{2v} structure when an electron is removed. The structure undergoes a shift with the same symmetry upon electron attachment, while it undergoes vast change upon electron removal. The bent ($n = 2$) and tridimensional ($n = 3$) structure can delocalize excess electron density to a higher extent as a result of their geometry arrangements than the linear ($n = 2$) and planar ($n = 3$) structure. The ground states are $5d^{10}$, $5d^{10}6s^1$ and $5d^{10}6s^2$ for Au^+, Au and Au^-, respectively. In the cation system, the $5d$ shell and in the neutral and anion systems the $6s$ electron shells interact with the Xe atoms, it results the geometry shift in the anion systems and vast change in the cation systems compared to its neutral state. The present systems have decreased energy gaps upon electron attachment and increased gap upon electron removal. The clusters have an improved capacity to donate electron as a result of their decreased HOMO–LUMO energy gaps.

3.3 NBO analysis

3.3.1 *Anion systems*

For the anion systems, the main contribution is the LP(Au) → RY*(Xe) donor–acceptor interactions, for $AuXe^-$, the LP of Au interact with different RY* orbits of Xe atom and the second order energies are 4.86, 3.43, 3.42, 3.25 kcal/mol, respectively. The natural population analysis in Table 1 clearly shows that more charge transfer occurred for larger anion systems, even so, there is only 0.0045 charge transferred from Au to each Xe atom for $AuXe_3{}^-$, the excess electron is kept with in the Au atom.

Table 3 The natural atomic orbital occupancies (the electron change value larger than 0.01) and natural electron configuration calculated at CCSD(T) theoretical level

Size	Natural atomic orbital occupancies		Natural electron configuration	
$n = 1$				
Anion			Au $6s^{2.00}5d^{10.00}$	Xe $5s^{2.00}5p^{6.00}$
Neutral(α)			Au $6s^{0.99}5d^{5.00}$	Xe $5s^{1.00}5p^{3.00}$
Neutral(β)	Au $6s^{0.01975}$	Xe $5p_z^{0.98408}$	Au $6s^{0.02}5d^{5.00}$	Xe $5s^{1.00}5p^{2.98}$
Cation	Au $6s^{0.17451}$	Xe $5p_z^{1.85149}$	Au $6s^{0.17}5d^{9.96}7p^{0.01}$	Xe $5s^{1.99}5p^{5.84}6d^{0.01}$
$n = 2$				
Anion			Au $6s^{1.99}5d^{10.00}$	Xe $5\mathrm{s}^{2.00}5p^{6.00}$
Neutral(α)	Au $6s^{0.98640}$		Au $6s^{0.99}5d^{5.00}7p^{0.01}$	Xe $5s^{1.00}5p^{3.00}$
Neutral(β)	Au $6s^{0.03641}$		Au $6s^{0.04}5d^{5.00}$	Xe $5s^{1.00}5p^{2.98}$
Cation	Au $6s^{0.48577}5d_{z^2}^{1.90347}$	Xe $5s^{1.9689}5p_z^{1.8154}$	Au $6s^{0.49}5d^{9.90}$	Xe $5s^{1.97}5p^{5.81}$
$n = 3$				
Anion	Au $6s^{1.98423}$		Au $6s^{1.98}5d^{10.00}$	Xe $5s^{2.00}5p^{6.00}$
Neutral(α)	Au $6s^{0.98064}$		Au $6s^{0.98}5d^{5.00}7p^{0.01}$	Xe $5s^{1.00}5p^{3.00}$
Neutral(β)	Au $6s^{0.04749}$		Au $6s^{0.05}5d^{5.00}$	Xe $5s^{1.00}5p^{2.99}$
Cation	Au $6s^{0.3955}6p_z^{0.0178}7p_y^{0.01850}5d_{x^2-y^2}^{1.96125}$		Au $6s^{0.40}5d^{9.95}6p^{0.02}7p^{0.02}$	
	Xe_{top} $5\mathrm{s}^{1.98512}5\mathrm{p}_z^{1.92045}$		Xe_{top} $5s^{1.99}5p^{5.92}$	
	Xe_{bot} $5s^{1.97362}5p_y^{1.88321}5p_z^{1.98385}$		Xe_{bot} $5s^{1.97}5p^{5.86}6d^{0.01}$	

3.3.2 Neutral systems

According to the second order energies $\Delta E^{(2)}$ for the most significant NBO donor–acceptor interaction analysis collected in Table 4, the most important contribution to the stabilization energy of the neutral systems is the LP(Au) → RY*(Xe) interactions. As can be seen from Table 4, the beta orbit donor–acceptor interaction contributions, are more than two times larger than that of alpha orbits. It can be seen (Table 3) that there is more charge transfer from Xe atom to Au atom of beta orbits than that of alpha orbits. We noticed that the donor–acceptor interaction of alpha and beta orbits decreased from $n = 1$ to $n = 3$. Natural atomic orbital occupancies indicate that the average charges transferred from Xe atom to the Au 6*s* orbits are 0.01975, 0.01821 and 0.01583 for $n = 1$, 2, and 3, respectively; and it result the decrease of the donor-acceptor interactions.

3.3.3 Cation systems

The NBO results show that there is one Au–Xe bond in each cation system. Each NBO bond (σ_{AB}) can be written in terms of two directed valence hybrids, h_A and h_B, on the bonded centers A and B, respectively; that is, $\sigma_{AB} = c_A h_A + c_B h_B$. The coefficients c_A and c_B vary smoothly from the covalent ($c_A = c_B$) to ionic limit ($c_A \gg c_B$). The bonding orbital can be expressed as

$$\sigma_{\text{AuXe}} = 0.9616\, h_{\text{Xe}} + 0.2744\, h_{\text{Au}} \qquad (n = 1)$$

$$\sigma_{\text{AuXe}_{\textcircled{2}}} = 0.9423 h_{\text{Xe}} + 0.3347 h_{\text{Au}} \qquad (n = 2)$$

$$\sigma_{\text{AuXe}_{\text{bot}-\textcircled{2}}} = 0.9572 h_{\text{Xe}} + 0.2894 h_{\text{Au}} \qquad (n = 3).$$

Table 4 Second order energies $\Delta E^{(2)}$ (Kcal/mol) for the most significant NBO donor-acceptor interactions (larger than 2.0 kcal/mol for anion and neutral systems, larger than 4.0 kcal/mol for cation systems) calculated at CCSD(T) theoretical level

	Donor → Acceptor						
Neutral							
$n = 1$	LP(Au) → RY*(Xe)	3.86	LP(Xe) → LP*(Au)	7.83			
$n = 2$	LP(Au) → RY*(Xe①)	3.44	LP(Xe①) → LP*(Au)	7.70			
	LP(Au) → RY*(Xe②)	3.44	LP(Xe②) → LP*(Au)	7.70			
$n = 3$	LP(Au) → RY*(Xe①)	3.35	LP(Xe①) → LP*(Au)	7.06			
	LP(Au) → RY*(Xe②)	3.35	LP(Xe②) → LP*(Au)	7.06			
	LP(Au) → RY*(Xe③)	3.35	LP(Xe③) → LP*(Au)	7.06			
Anion							
$n = 1$	LP(Au) → RY*(Xe)		4.86	3.25	3.42	3.43	(14.96)
$n = 2$	LP(Au) → RY*(Xe①)		3.37	2.37	2.13		(7.87)
	LP(Au) → RY*(Xe②)		3.37	2.37	2.13		(7.87)
$n = 3$	LP(Au) → RY*(Xe①)		4.69	2.60	2.80	2.68	(12.77)
	LP(Au) → RY*(Xe②)		4.69	2.30	2.90	2.68	(12.57)
	LP(Au) → RY*(Xe③)		4.69	2.30	2.90	2.68	(12.57)
Cation							
$n = 1$	LP(Au) → RY*(Xe)		4.42				(4.42)
$n = 2$	BD*(Au–Xe②) → RY*(Au)		14.17	12.99	4.13		(31.29)
	BD*(Au–Xe②) → RY*(Xe②)		7.31	5.12	4.23		(16.66)
	LP(Xe①) → RY*(Au)		22.49	19.86	7.23	4.95	(54.53)
	LP(Xe①) → RY*(Xe②)		9.79	4.56			(14.35)
	LP(Xe①) → BD*(Au–Xe②)		118.12				(118.12)
	LP(Xe①) → RY*(Xe①)		7.38	4.29			(11.67)
$n = 3$	BD*(Au-Xe$_{\text{bot-②}}$) → RY*(Au)		12.18	13.44	6.02	5.26	(36.90)
	BD*(Au-Xe$_{\text{bot-②}}$) → RY*(Xe $_{\text{bot-②}}$)		7.27	6.11	5.50	4.71	(23.59)
	LP(Xe$_{\text{top}}$) → BD*(Au-Xe $_{\text{bot-②}}$)		37.28				(37.28)
	LP(Xe$_{\text{top}}$) → RY*(Au)		5.90	5.16	5.00	4.14	(20.20)
	LP(Xe$_{\text{bot-①}}$) → BD*(Au-Xe $_{\text{bot-②}}$)		70.19				(70.19)
	LP(Xe$_{\text{bot-①}}$) → RY*(Au)		13.05	11.19	9.61		(33.85)

Considering that the bonding strength is proportion to the electron donation, based on the NBO analysis, we can concluded that the Au^{+}–Xe bond is a polar dative bond, closer to the covalent than the ionic limit.

For $n = 1$, h_{Xe} and h_{Au} can be described as linear combination of the natural atomic orbitals on its center as follows:

$$h_{\mathrm{Xe}} = 0.303(5s) + 0.9506(5p_z)$$

$$h_{\mathrm{Au}} = 0.9649(6s) - 0.2163(7p_z) + 0.1277(5d_{z^2}).$$

From Table 3, we can see that the orbital occupancies of $5p_z$(Xe) and $6s$(Au), 1.85149 and 0.17451, show that about 0.175 charge transfer from $5p_z$(Xe) to $6s$(Au) for AuXe^{+}. For AuXe$_2^{+}$, the bond between Au and Xe$_{②}$ resulting from the overlap of an *sd* (mainly d_{z^2}) hybrid on Au and *sp*(mainly p_z) hybrid on Xe$_{②}$ atom; it can be seen from the occupancies of the orbits given in Table 3, $6s^{0.48577}5d_{z^2}^{1.90347}$ for Au and $5s^{1.9689}5p_z^{1.8154}$ for Xe$_{②}$. For AuXe$_3^{+}$, the NBO coefficients show that the $5s$, $5p_y$, $5p_z$ (mainly $5p_y$) orbits of Xe$_{\text{bot-②}}$ atom and the $6s$, $7p_y$, $5d_{x^2-y^2}$ orbits of Au participate in the bond and the natural atomic orbital occupancies collected in Table 3 also sustain it.

For AuXe^{+}, the main interaction is LP(Au) → RY*(Xe) except for the Xe–Au^{+} bond mentioned above. The interactions become more complicated upon the Xe atom addition. For AuXe$_2^{+}$, the most important source of stabilization is the LP(Xe$_{①}$) → BD*(Au–Xe$_{②}$) donor–acceptor interactions and other contributions mainly come from the LP(Xe$_{①}$) → RY*(Au) and BD*(Au–Xe$_{②}$) → RY*(Au), it indicates that charge transfers between the lone pairs of Xe$_{①}$ and the anti-bonding orbits, Rydberg orbits of Au are important.

For AuXe$_3^{+}$, the most contribution comes from the interaction between the lone pair of Xe$_{\text{bot-①}}$ and the anti-bonding orbit of Au–Xe$_{\text{bot-②}}$. One can see from the donor–acceptor interactions collected in Table 4 that charge transfer from both Xe$_{\text{top}}$ and Xe$_{\text{bot-①}}$ to the Au–Xe$_{\text{bot-②}}$ bonding unit. The natural atomic orbital occupancies and natural electron configuration of AuXe$_3^{+}$ collected in Table 3, also show charge transferred from $5p_z$ orbit of Xe$_{\text{top}}$ and $5p_y$ orbit of Xe$_{\text{bot-①}}$. Within the Au–Xe$_{\text{bot-②}}$ bonding unit, the donor–acceptor interaction of anti-bonding orbit and Rydberg orbits of Au and Xe$_{\text{bot-②}}$ are also very important contributions to the stabilization energy of the system. The Xe$_{\text{bot-①}}$ and Xe$_{\text{bot-②}}$ are in the equivalent position and have the same natural atomic orbital occupancies $5s^{1.97362}5p_y^{1.88321}5p_z^{1.98385}$, which indicate that there is 0.12 charge transferred from $5p_y$ orbit to Au–Xe$_{\text{bot-②}}$ bonding unit for Xe$_{\text{bot-①}}$, whereas to Au $6s$ orbit from Xe$_{\text{bot-②}}$ when the Au–Xe$_{\text{bot-②}}$ bond come into being.

The weak LP(Xe) → LP*(Au) and LP(Au) → RY*(Xe) donor–acceptor interactions play an important role in the contribution to the stabilization energy for the neutral and anion system, respectively, and there is almost no charge transfer occurred. The neutrals are van der Waals complexes and the anions are a little more strongly bound. While there are strong interactions for the cation systems, the donor–acceptor interactions become more complicated and more charge transfer occurred, the charge transfer from Xe to Au might serve as a characteristic parameter of the interactions. The main future of the interaction is a charge accumulation in the middle of the region between the Au and Xe nuclei.

4 Conclusion

We investigated the AuXe$_n^Z$ (n = 1–3, $Z = -1$, 0, +1) cluster series by quantum calculations at CCSD(T) theoretical level with extended basis sets, providing the reliable structure, stabilities and the nature of the interactions. The geometry structure modifies its geometry upon electron addition or removal, the anion have similar structures with same symmetry as its neutrals, whereas there are vast changes for the cation series. The stabilities increase with the cluster size for all systems; the cations have stronger stabilities than neutrals and anions.

The natural bond orbital analysis, atomic orbital occupancies, natural population and donor–acceptor interactions analysis clear show that:

1. There is one Au–Xe bond in each cation system. The main mode of density transfer is from a filled $5p$ orbit of the Xe into the $6s$ of Au atom.
2. The LP of the non-bonded Xe atom(s) → the anti-bonding orbit of the Au–Xe bonding unit donor-acceptor interaction, and the LP(Xe) → RY*(Au) interaction dominate the interactions of cation systems. There is significant charge transfer occurred between the Xe atom(s) and the Au–Xe bonding unit. The charge transferred from Xe to Au may serves as a characteristic parameter of the interaction.
3. The LP(Xe) → LP*(Au) donor–acceptor interactions dominate in the neutral systems and charge transferred from Xe atom to Au atom. For the anion systems, the LP(Au) → RY*(Xe) come in to play and charge transferred from Au^{-} to Xe atom. The charge transfer can be negligible for both systems.

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