Minimum Polarizability Principle Applied to Lowest Energy Isomers of Some Gaseous All-Metal Clusters

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In comparison with the minimum energy criterion as an indicator of the most stable state, the minimum polarizability and maximum hardness principles have been examined to describe the relative stability of various isomers of nine gaseous all-metal clusters M_4X^- (Cu_4Na^-, Cu_4Li^-, Al_4Cu^-, Ag_4Li^-, Au_4Li^-, Ag_4Na^-, Au_4Na^-, Al_4Ag^-, Al_4Au^-) on the basis of MP2 calculations. In these species, there are two lowest energy isomers with near isoenergy that sometimes make it very difficult to determine which of them is more stable when we depend only on the minimum energy criterion. According to the minimum polarizability principle, however, the square-pyramidal structure is always more stable than the planar isomer at various computational levels, which was also confirmed by the results from the minimum energy principle that sometimes requires higher computational precision. Thus, there is an indication that, at least for our present cluster system, the minimum polarizability principle is less dependent on the computational levels compared to the minimum energy principle.

1. Introduction

As recently reported in *Science*, there are three gaseous all-metal aromatic clusters M_4Al^- (M = Li, Na, Cu) that have been produced by the laser vaporization technique and characterized by the combined study of photoelectron spectra and ab initio calculations.[1] For this special class of all-metal clusters with unusual stability there are two low-lying isomers with near isoenergy, the square-pyramidal isomer (a) and the square-capped planar isomer (b) (Figure 1), where the former has been proven to be the minimum energy structure at both the second-order Møller-Plesset perturbation (MP2) level[2−4] and the coupled cluster (CC) level.[5,6] Since then, the correlation ab initio method has become a common and powerful tool to determine the molecular architectures, bonding behavior, and aromatic characteristics of various gaseous all-metal clusters since the large activities of some gaseous species make it very difficult for the experiments to measure molecular structures.[1,7−9]

Due to the discovery of an abundance of gaseous all-metal clusters, an advance has recently been published in *Chemical Reviews* where the aromatic/antiaromatic features of some ring-shaped all-metal clusters are highlighted.[10] The generally accepted concept is that ring-shaped metal clusters with $(4n + 2)$ π electrons, for example, Al_4^{2-} and Hg_4^{6-}, can be aromatic.[1,11−13] With the help of ab initio calculations with high precision it has been revealed that a number of all-metal four-numbered-ring (M_4^{2-}) moieties possess double aromaticity since both σ and π orbitals sustain diatropic ring currents, as observed in M_4Na^- and M_4Na_2 (M = Al, Ga, In, Sb, Bi, Cu).[1,8,11,12,14,15]

However, some challenging problems have recently emerged in determining the minimum energy structures and the relative energies of various isomers of some all-metal clusters. An example is the M_4Li^- (M = Cu, Ag, Au) clusters.[8] Although it was exhibited that the square-pyramidal isomer (a) with C_{4v} symmetry is the lowest energy structure in terms of molecular geometry optimization at the MP2/TZVPP level, single-point calculations at the CCSD and CCSD(T) levels suggest that the fanlike-planar isomer (c) with C_{2v} symmetry seems to be the most stable (Figure 1). In the present work, we made great efforts to detect which isomer finally belongs to the lowest energy structure. In addition, for the Au_4Na^- cluster we noticed that although the planar isomer (c) is lower in energy than the pyramidal isomer (a) at the MP2 level with smaller basis sets, the pyramidal isomer (a) becomes the lowest energy structure at the MP2 level with larger basis sets. The other motivation to write the present paper is that we want to confirm that the pyramidal isomer (a) of the Au_4Al^- cluster is the lowest energy structure. In previous work,[9] with the Gaussian 98 program[16] we optimized one approximately planar pyramidal isomer (a) of the Au_4Al^- cluster with a height of 0.034 Å and width of 3.572 Å, which is less stable than the planar isomer (b). In the present work, with the Gaussian 03 program[17] we optimized one ordinary square-pyramidal isomer (a) with a height of 1.649 Å and width of 2.739 Å, which is the lowest energy structure. The discrepancy derives probably from the improvement of the Gaussian program since the Harris guess has been adopted as the default initial guess in Gaussian 03.

As it is known, the minimum energy principle is the ultimate criterion to detect which configuration is the most stable whereas the minimum polarizability and maximum hardness principles require further examination of the description of various chemical systems. The concept of hardness was first presented in 1951 with the definition of the hard−soft acid−base principle.[18,19] Subsequently, Pearson described the maximum hardness principle as “there seems to be a rule of nature that molecules arrange themselves so as to be hard as possible”.[20,21] The minimum polarizability principle presented by Chattaraj and Sengupta states a possibility as “the natural direction of

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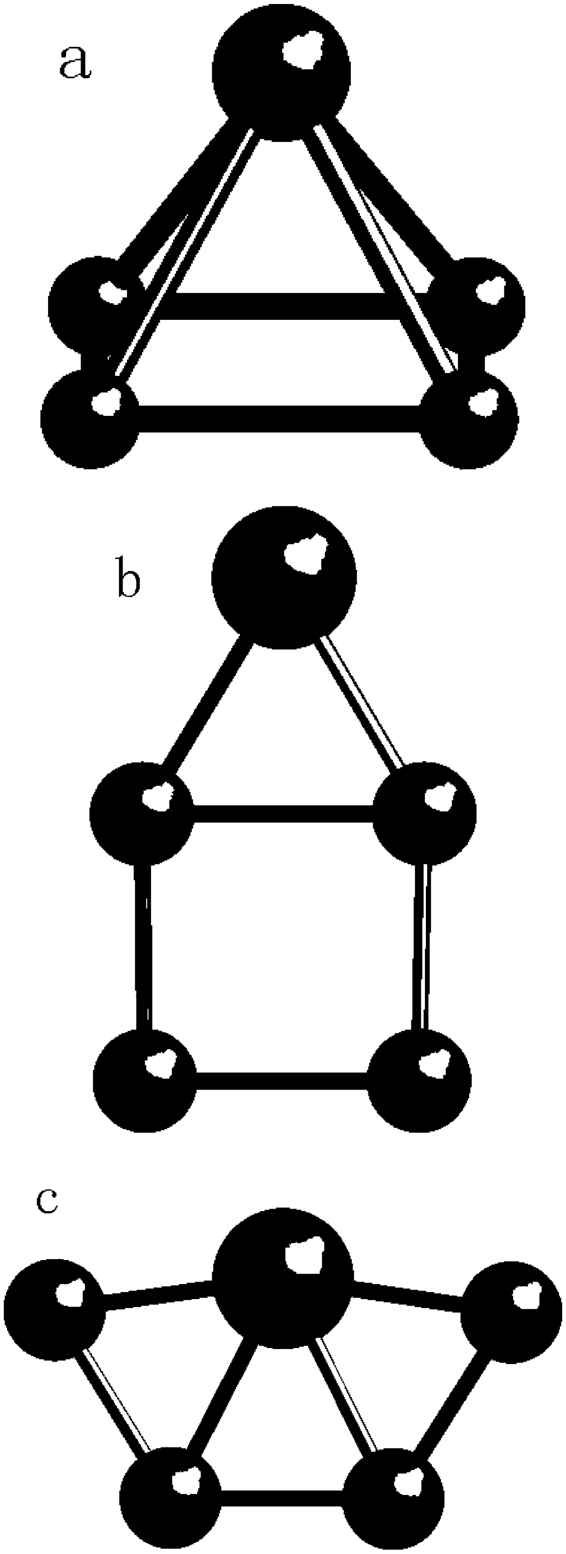

Figure 1. Pyramidal isomer (a) and capped-square planar isomer (b) of Al_4Cu^-, Al_4Ag^- and Al_4Au^-, and pyramidal isomer (a) and fanlike-planar isomer (c) of Cu_4Li^-, Cu_4Na^-, Ag_4Li^-, Au_4Li^-, Ag_4Na^-, and Au_4Na^-.

evolution of any system is towards a state of minimum polarizability".[22,23] On the basis of the definitions of the minimum polarizability and maximum hardness principles, Chattaraj and Maiti concluded "in general, a stable state (minimum energy configuration) or a favorable process is associated with the maximum hardness and minimum polarizability".[24]

Recently, Chattaraj and co-workers applied the maximum hardness and minimum polarizability principles to various possible isomers of Al_4^{2-} and Al_4^{4-} species, suggesting that the most stable isomer with the minimum energy is the hardest and least polarizable.[11,12,25] In our previous paper,[9] it was shown that the minimum polarizability principle rather than the maximum hardness principle is worth using in assessing the relative stability of various isomers of some gaseous all-metal clusters since the relative stability of various isomers of the MAl_4^- ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$) clusters can be well predicted by the minimum polarizability principle. In addition, for the MAl_4^{2-} ($M = Cu^+, Ag^+, Au^+$) clusters, it has been illuminated that the minimum polarizability principle is rather satisfactory whereas the maximum hardness principle is not valid enough.

Presently, there seems to be a viewpoint that the minimum polarizability principle is likely to become a tool to search for the lowest energy structure of various gaseous all-metal clusters. As we noticed in the current work, since the polarizability of the pyramidal isomer is always smaller than the planar isomer for the present nine clusters, the pyramidal isomer will be more stable on the condition that the minimum polarizability principle is reasonable. This conclusion has been further supported by the results from the minimum energy principle that sometimes requires higher computational precision. In other words, although the minimum energy principle is an ultimate criterion in determining the relative stability of various isomers, the validity of its calculated results depends more on the computational level. On the other hand, the minimum principle can more readily give the correct conclusion for which isomer is more stable, even at the rather low computational levels.

2. Computational Methods

For a chemical system, chemical hardness (η) is defined as

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_V \tag{1}$$

where E is the total energy, N is the total electron number, and V is the constant external potential.[22,27] With the finite differential approach and Koopman's theorem η can read

$$\eta = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} \tag{2}$$

after half factors in the right-hand side of the original equation have been omitted.[28]

In the previous letter,[9] we defined in detail the three descriptors for the relative stability between the pyramidal (C_{4v}) and planar (C_{2v}) isomers as

$$\Delta E = E(C_{2v}) - E(C_{4v}) \tag{3}$$

$$\Delta\eta = \eta(C_{4v}) - \eta(C_{2v}) \tag{4}$$

$$\Delta\alpha = \alpha(C_{2v}) - \alpha(C_{4v}) \tag{5}$$

where the positive magnitudes of relative energy (ΔE), relative hardness ($\Delta\eta$), and relative polarizability ($\Delta\alpha$) should imply that the pyramidal isomer is more stable when the minimum energy, maximum hardness, and minimum polarizability principles are reasonable.

According to Buckingham's equation,[29] the diagonal tensor component (α_{ii}) of the linear electric polarizability describes the linear response property of the electron density of a

TABLE 1: Relative Polarizability (Δα, in au), Relative Hardness (Δ*η*, in kcal/mol), and Relative Energy (Δ*E*, in kcal/mol) between Two Low-Energy Isomers of Al_4Cu^-, Cu_4Li^-, and Cu_4Na^- at the MP2 Level

	Al_4Cu^- [a]			Cu_4Li^- [b]			Cu_4Na^- [c]		
	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE
3-21G	79	5.7	20.37	17	0.5	38.39	53	−15.3	50.64
3-21G*	112	−2.6	39.91	17	0.5	38.39	35	−5.6	29.92
6-31G	31	5.3	10.11	21	−5.6	20.39	26	−15.8	18.81
6-31+G	17	15.6	15.51	13	13.2	3.63	22	2.2	0.12
6-31G*	55	2.5	24.49	18	−3.4	17.78	30	2.4	−0.00
6-31+G*	32	14.5	15.03				17	−11.5	17.42
6-311G	27	6.7	6.14	15	3.9	−3.55	26	−5	−9.93
6-311+G	20	18.1	15.24	16	9.1	3.78	27	0.1	−0.25
6-311G*	28	7.0	18.02	6	3.5	−0.14	13	−3.5	−7.03
6-311+G*	33	16.6	12.57	6	9.4	4.99	25	0.7	0.99

[a] $\Delta E = 7.6$ kcal/mol at the MP2/6-311+G* level,[1] $\Delta E = 12.57$ kcal/mol at the MP2/6-311+G* level, and $\Delta E = 12.59$ kcal/mol at the MP2/6-311+G(2df) level.[9] [b] $\Delta E = 11.7$ kJ/mol (2.8 kcal/mol) at the MP2/TZVPP level.[8] [c] $\Delta E = -3.5$ kJ/mol (−0.8 kcal/mol) at the MP2/TZVPP level.[8] In the present work, $\Delta E = 1.9$ kcal/mol according to simple point calculations at the MP2/6-31++G(2df) level to the geometry optimized at the MP2/6-311+G* level.

molecular system with respect to an infinitesimal external electric field, F_i. With Kurtz's finite-field scheme[30]

$$\alpha_{ii} = \left\{\frac{5}{2}E(0) - \frac{4}{3}[E(F_i) + E(-F_i)] + \frac{1}{12}[E(2F_i) + E(-2F_i)]\right\}/F_i^2 \quad (6)$$

where the subscript *i* runs over Cartesian coordinate axes *x*, *y*, and *z* and $E(F_i)$ is the total energy of the molecular system. Generally, the experimentally measurable quality is the mean polarizability

$$\alpha = \frac{\sum \alpha_{ii}}{3} \quad (7)$$

With the Gaussian 03 package[17] the two low-lying isomers of each cluster are optimized with the MP2 method with various basis sets. In Figure 1, three low-lying isomers previously reported are the square-pyramidal (C_{4v}) structure (a), the square-capped planar (C_{2v}) structure (b), and the fanlike planar (C_{2v}) structure (c). Isomers a and b are the lowest energy structures of the Al_4Cu^-, Al_4Ag^-, and Al_4Au^- clusters and isomers a and c are the lowest energy structures of the Cu_4Na^-, Cu_4Li^-, Ag_4Li^-, Au_4Li^-, Ag_4Na^-, and Au_4Na^- clusters.[1,8]

In previous calculations application of the complete basis sets 6-31+G* and 6-311+G* and the effective core potential (ECP) relativistic basis set SBKJC were satisfactory.[1,9] In the present work, the calculated results of the Cu_4Na^-, Cu_4Li^-, and Al_4Cu^- clusters are listed in Table 1, where 10 all-electron basis sets from 3-21G to 6-311+G* are utilized for the geometry optimizations without symmetry constraint. Subsequently, the parameters *η* and α and the descriptors Δ*E*, Δ*η*, and Δα were calculated at the same computational levels as the geometry optimizations. It is required to point out that our present calculations are different from the previous practices that carried out single-point calculations to some given geometries.[8,9]

For the other clusters in Tables 2−4 the 6-311+G* basis set is employed for Na, K, and Al. Six ECP basis sets as LanL2DZ, LanL2DZ+f, SBKJC, SBKJC+f, Stuttgart, and Stuttgart+f are utilized for heavy elements. LanL2DZ is a Los Alamos ECP plus double-ζ (DZ) split basis,[31−33] SBKJC is a 21G relativistic ECP basis,[34−36] and Stuttgart is a relativistic and small core ECP basis.[37−38] The basis sets LanL2DZ+f, SBKJC+f, and Stuttgart+f are augmented with one f polarization function with a coefficient of 3.525 for Cu, 1.611 for Ag, and 1.05 for Au, respectively.

TABLE 2: Relative Polarizability (Δα, in au), Relative Hardness (Δ*η*, in kcal/mol), and Relative Energy (Δ*E*, in kcal/mol) between Two Low-Energy Isomers of Ag_4Li^-, Au_4Li^-, and Ag_4Na^- at the MP2 Level

	Ag_4Li^- [a]			Au_4Li^- [b]			Ag_4Na^- [c]		
	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE
LanL2DZ	26	4.0	1.97	11	−0.4	1.81	24	−1.9	−0.95
LanL2DZ+f	19	4.5	3.71	10	−0.6	5.56	23	−1.8	1.10
SBKJC	21	3.6	2.48	12	0.3	1.35	31	−0.6	−0.72
SBKJC+f	16	3.9	3.48	10	0.0	3.25	40	−0.5	0.52
Stuttgart	52	7.6	3.36	6	4.0	1.04	27	−1.8	0.13
Stuttgart+f	8	8.0	4.83	2	3.9	3.23	23	−1.4	1.78

[a] $\Delta E = 12.4$ kJ/mol (3.0 kcal/mol) at the MP2/TZVPP level.[8] [b] $\Delta E = 0.6$ kJ/mol (0.1 kcal/mol) at the MP2 level using TZVPP for Na and 7s5p3d2f for Au.[8] [c] $\Delta E = -3.0$ kJ/mol (−0.7 kcal/mol) at the MP2/TZVPP level.[8]

TABLE 3: Relative Polarizability (Δα, in au), Relative Hardness (Δ*η*, in kcal/mol), and Relative Energy (Δ*E*, in kcal/mol) between Two Low-Energy Isomers of Au_4Na^-, Al_4Ag^-, and Al_4Au^- at the MP2 Level

	Au_4Na^- [a]			Al_4Ag^- [b]			Al_4Au^-		
	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE	$\Delta\alpha$	$\Delta\eta$	ΔE
LanL2DZ	15	−5.4	−2.01	36	13.9	5.25	22	7.0	1.44
LanL2DZ+f	17	−5.8	2.74	35	14.6	7.42	19	6.8	5.61
SBKJC	17	−4.9	−2.51	34	10.8	5.01	20	6.6	1.66
SBKJC+f	19	−5.2	−0.04	32	9.5	7.15	13	6.8	6.30
Stuttgart	10	0.3	−3.65	33	13.1	6.24	20	3.4	2.20
Stuttgart+f	9	0.2	−0.98	31	13.8	9.12	24	4.5	6.45

[a] $\Delta E = -17.9$ kJ/mol (−4.3 kcal/mol) at the MP2/TZVPP level.[8] [b] Data of Al_4Ag^- at the MP2/SBKJC+f level were taken from the literature.[9]

TABLE 4: Polarizability Difference (Δα, in au), Hardness Change (Δ*η*, in kcal/mol), and Relative Energy (Δ*E*, in kcal/mol) of Isomers of Cluster Au_4Na^- at the Higher Basis Set Levels

isomer	a		c				
parameter	α	η	α	η	$\Delta\alpha$	$\Delta\eta$	ΔE
LanL2DZ+2*f*	222	89	240	95	18	−6	4.13
SBKJC+2*f*	190	86	211	91	21	−5	0.96
Stuttgart+2*f*	203	81	225	82	22	−1	0.80

In Table 3 we notice that the Δ*E* value of the Au_4Na^- cluster is large and positive at the LanL2DZ+f level but negative at the computational levels of the other basis sets. Thus, further calculations are required to confirm which result is correct. In Table 4 application of the larger basis sets leads uniformly to the positive Δ*E* magnitude, where the basis sets LanL2DZ+2f, SBKJC+2f, and Stuttgart+2f derive, respectively, from addition of one f diffuse function of Au with a coefficient of 0.43 to the LanL2DZ+f, SBKJC+f, and Stuttgart+f basis sets.

3. Results and Discussion

In Table 1 all the large magnitudes of Δα illuminate that it is difficult to change the positive sign of Δα by varying the basis set. Although Δ*E* and Δ*η* have no trend in both sign and magnitude, the positive values at the highest MP2/6-311+G* level suggest that the pyramidal isomer is more stable.

The simplest case is Al_4Cu^-, which possesses large and positive values of Δα and Δ*E*. This is in agreement with the previously reported Δ*E*, 7.6 kcal/mol at the MP2/6-311+G* level,[1] 12.57 kcal/mol at the same level of theory,[9] and 12.59 kcal/mol at the MP2/6-311+G(2df) level.[9] Undoubtedly, the pyramidal isomer of Al_4Cu^- is the lowest energy structure. This conclusion has been supported by comparison between the experimentally measured and theoretically simulated photoelectron spectra since the experimental photoelectron spectra can better agree with the calculated results for the pyramidal species.[1] For $\Delta\eta$, however, the negative value (−2.6 kcal/mol) at the MP2/3-21G* level suggests that this descriptor is not ideal enough to describe the relative stability.

For Cu_4Li^-, although the converged geometry has not been obtained at the MP2/6-31+G* level, the magnitude of ΔE, 4.99 kcal/mol at the MP2/6-311+G* level, indicates that the pyramidal isomer is more stable than the planar isomer. Lin and Wang reported the positive value of ΔE at the MP2/TZVPP level, 2.8 kcal/mol, and the larger extrapolated result from single-point calculations at the CCSD(T)/QZVPP level, 7.4 kcal/mol.[8] Actually, our $\Delta\alpha$, ΔE, and $\Delta\eta$ are so large and positive at the MP2/6-311+G* level that the pyramidal isomer of Cu_4Li^- is really much more stable.

For Cu_4Na^-, although the positive values of $\Delta\alpha$ show that the pyramidal isomer is more stable than the planar species, it is very difficult to determine which isomer is more stable in terms of ΔE and $\Delta\eta$. Although ΔE is positive at the higher computational levels, 17.42 kcal/mol at the MP2/6-31+G* level and 0.99 kcal/mol at the MP2/6-311+G* level, it is probably negative after the zero-point energy correction since the ΔE value at the 6-311+G* level is so small and much smaller than that at the MP2/6-31+G* level. Thus, it is required to further confirm the question. Since single-point calculations at the MP2/6-311++G(2df) level to the geometry optimized at the MP2/6-311+G* level give a larger ΔE, 1.9 kcal/mol, compared to the result at the MP2/6-311+G* level, we believe that the pyramidal isomer is more stable. In fact, our calculated results are in agreement with those reported by Lin and Wang.[8]

In Table 2 all the large and positive values of $\Delta\alpha$ and ΔE of Ag_4Li^- and Au_4Li^- indicate that the pyramidal isomer is more stable. The calculated results of the two clusters are in agreement with the previous conclusion reported by Lin and Wang, where the positive value of ΔE is 3.0 kcal/mol for Ag_4Li^- and 0.1 kcal/mol for Au_4Li^- at the MP2/TZVPP level.[8] As for Ag_4Na^-, although the ΔE value is negative at the MP2/LanL2DZ and MP2/SBKJC levels, it becomes positive when one f polarization function is added to LanL2DZ and SBKJC. Thus, the pyramidal isomer is still more stable. As for $\Delta\eta$, various cases have emerged that are all positive $\Delta\eta$ for Ag_4Li^-, positive or negative $\Delta\eta$ for Au_4Li^-, and all negative $\Delta\eta$ for Ag_4Na^-. Thus, this descriptor is not a good enough index to describe the relative stability of various isomers.

In Table 3 the simplest case is Al_4Ag^- and Al_4Au^- since all the large and positive values of $\Delta\alpha$ and ΔE show that the pyramidal isomer has the minimum energy. The most intricate and challenging situation occurs in Au_4Na^-. Note that all the values of $\Delta\alpha$ are positive whereas the values of ΔE are negative, with the exception of ΔE at the LanL2DZ+f level, 2.74 kcal/mol. Lin and Wang also reported a negative value of ΔE, −4.3 kcal/mol at the MP2/TZVPP level.[8] The planar isomer seems to be more stable. This conclusion was also supported by the comparison between experimental and simulated photoelectron spectra. However, we wonder how to interpret the large and positive magnitude of ΔE at the MP2/LanL2DZ+f level. Moreover, when one f polarization function is added to SBKJC and Stuttgart, the value of ΔE shifts toward the positive direction from −2.51 to −0.04 kcal/mol for the former and −3.65 to −0.98 kcal/mol for latter, respectively.

In Table 4 all ΔE values of Au_4Na^- become positive when the larger basis sets such as LanL2DZ+2f, SBKJC+2f, and Stuttgart+2f are used to optimize the geometric structure. The result at the MP2/LanL2DZ+2f level, $\Delta E = 4.13$ kcal/mol, is so large that it is difficult to change the sign of ΔE by the zero-point energy corrections. Thus, the pyramidal isomer of this cluster is still the lowest energy structure, which is different from the results previously reported by Li and Wang.[9] Although it will be very important how to interpret the difference between the previous and prevent results,[8] it seems to be subject to the content of another paper in which photoelectron spectra should be well simulated.

Summarily, the positive values of $\Delta\alpha$ indicate that the pyramidal isomer is always more stable than the planar isomer on the condition that the minimum polarizability principle is reasonable. Since the signs of $\Delta\eta$ and ΔE are probably changed with varying the basis set, it is sometimes difficult to determine which isomer is more stable by means of the maximum hardness and minimum energy principles. The positive values of ΔE at the levels of the larger basis sets, however, show that the pyramidal isomer still is more stable and give strong support to the minimum polarizability principle.

4. Conclusions

In the present work, we systemically assessed the behavior of the minimum polarizability and maximum hardness and minimum energy principles to describe the two low-lying isomers of nine M_4X^- bimetal clusters in light of the MP2 calculations. The results show that, at least for our present species, the pyramidal isomer possesses smaller polarizability and lower energy than the planar structure. In other words, the pyramidal isomer is more stable. In addition, the minimum polarizability principle depends less on the computational level, so it is worth being recommended in the search for the minimum energy structure of gaseous all-metal clusters. However, further work should be done before this principle can serve as one criterion of the relative stability for various isomers of different chemical systems.

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