

Ab initio study on the aromaticity of all-metallic anion La_4^{2-}

Yong Liu^a, Ming Xiao^a, Huai-Xing Wang^a, and Xian-Xing Chi^{b,*}

^a Department of Physics and Electronics, Hubei University of Education, Wuhan 430205, China

^b School of Physics and Electronic Information, Wenzhou University, Wenzhou 325027, China

Received 12 March 2013; Accepted (in revised version) 26 May 2013

Published Online 18 November 2013

Abstract. We extended the aromaticity concept to all-metallic anion La_4^{2-} and then performed Ab initio calculations (B3LYP/LANL2DZ, B3PW91/LANL2DZ and MP2/LANL2DZ) on the selected structures. The computed results indicate that anion La_4^{2-} has two stable isomers: one is the bidentate C_{2v} structure and another is the square planar D_{4h} structure. The further analysis on energies shows that the square planar D_{4h} structure is more stable than the bidentate C_{2v} structure. The computed nucleus-independent chemical shifts (NICS) on the most stable D_{4h} structure show that the square planar La_4^{2-} ring exhibits higher degree of aromaticity. The detailed MOs analysis further reveals that the square planar La_4^{2-} ring possesses four independent delocalized bonding systems, each has two electrons satisfying the $4n + 2$ electron counting rule of aromaticity, suggesting that these species have four-fold aromaticity.

PACS: 31.10.+z, 31.15.Ar, 31.15.Ew

Key words: *ab initio* study, aromaticity, magnetic susceptibilities, nucleus-independent chemical shift (NICS)

1 Introduction

The concept of aromaticity is one of the most significant concepts in traditional chemistry. It is generally used to describe cyclic, planar, and conjugated molecules with a simple two-center two-electron (2c-2e) bond model. Despite the undeniable usefulness of the aromaticity concept, its physical origin is still being controversially debated [1, 2]. The development of various criteria of aromaticity and theoretical investigations aimed

*Corresponding author. Email address: guqintai@21cn.com (Y. Liu)

at gaining a deeper insight into the origin of this phenomenon[3-5]. Some generally accepted criteria for aromaticity have been formulated and often used for identifying the aromaticity of molecules, like high energetical stability, cyclic planar geometries, and unusual magnetic properties such as magnetic susceptibilities [2]. Recently a new magnetic criterion, viz. Nucleus-Independent Chemical Shift (NICS), proposed by Schleyer *et al.*[4], was used to probe aromaticity. This criterion have been tested over a wide variety of molecules and found to be an efficient and simple criterion in evaluating the aromaticity, although some think that it is unreliable for measuring aromaticity [6], and a few difficult cases arise for NICS indicator of aromaticity.

For the last years the applicability of the aromaticity concept has been expanded to metallic clusters in a combined photoelectron spectroscopy and electronic structure computational investigation of all-metal molecules containing Al_3^- , Ga_3^- , XAl_3^- , Al_4^{2-} , Ga_4^{2-} , In_4^{2-} , Hg_4^{6-} , Al_5^- and Al_6^{2-} aromatic units[7-18]. All these systems are electron deficient species compared to the aromatic hydrocarbons. The electron deficiency results in an interesting new feature in metallic aromatic systems, which should be considered as having both σ and π aromaticity, and that should result in their additional stability. Boldyrev and Wang in a feature article[19] surveyed their pioneering work on the design and characterization of a number of nonstoichiometric Molecular and clusters species. Due to the more complicated nodal structure of d-AOs that can form δ -bond in addition to σ and π bonds, transition-metal systems can provide a more diverse array of aromaticity-antiaromaticity combinations. So far only few transition metal systems with d-AO based aromaticity have been reported [20-23]. These examples have already shown the usefulness of the aromaticity concept and we believe that the advances of the aromaticity concept further into metal and nonmetal clusters will help us better understand chemical bonding, structure, and stability of these species as well as serve as a better interpretation of spectroscopic data.

In this work, we investigate theoretically a new all-metal anionic La_4^{2-} consisting of transition metal atoms La, for which there is only one valence d-AO electron and two filled valence s-AO electrons. Compared with X_4^{2-} ($\text{X}=\text{B}$, Al , and Ga) species, the anionic cluster La_4^{2-} can be expected to possess the four independent delocalized bonding systems, rendering doubly σ and doubly π aromatic character originating primarily from d AOs of the transition metal atoms La. Meanwhile, resonance energies (RE) for the La_4^{2-} species are also investigated, which can provide some computational predictions for future possible experimental observation.

2 Computational methods

The structural optimization, vibration frequencies, the number of imaginary frequencies (NImag) and total energies (E_{tot}) of all-metallic La_4^{2-} clusters were calculated with three methods: B3LYP (Becke's three-parameter hybrid functional and Perdew and Wang's 1991 gradient-corrected correlation functional) [24, 25], B3PW91 (B3 and the non-local

correlation of Lee, Yang, and Parr) [26] and MP2 (second-order Møller-plesset perturbation method) [27, 28]. The effective core potential (ECP) of LANL2DZ basis set was adopted for the heavier metal atom Lanthanum ($Z=57$). The extended 6-311+G* basis set is used for the Na atom.

NICS method is a magnetic criterion that mirrors the ring current. In this method, the nuclear magnetic resonance (NMR) parameters are calculated for a ghost atom, usually placed at the centre of ring, and the NICS value is the negative of the isotropic magnetic shielding constant at the ghost atom. System with negative NICS values are aromatic, since negative values arise when diatropic ring current (shielding) dominates, whereas systems with positive values are antiaromatic because positive value arise when paratropic current (deshielding) dominates. Non-aromatic cyclic system should, therefore, have NICS values around zero. The more negative the NICS, the more aromatic the system is. In this study five NICS values are calculated at five positions in each of all-metal clusters: the center of the ring and points 0.5Å, 1.0Å, 1.5Å, 2.0Å above the center of the ring, which are denoted NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5), NICS(2.0) respectively.

All calculations in this work are performed using the Gaussian03 program[29]. The MO pictures are drawn using the Gaussview 3.0 program.

3 Results and discussion

3.1 The stable structures

The optimized geometric structures and the number of imaginary frequencies (NImag) for anion La_4^{2-} , NaLa_4^- and Na_2La_4 are illustrated in Fig. 1. Their total energies (E_{tot}) and geometric parameters are summarized in Table 1 and Table 2.

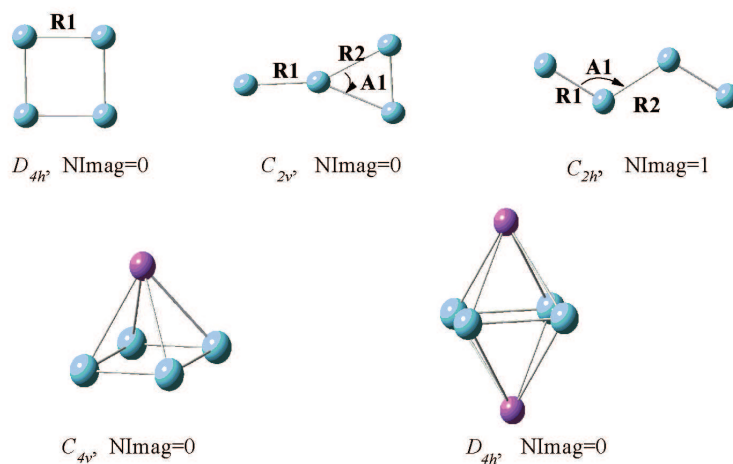
Table 1: Optimized geometric structures, total energies (E_{tot}) and relative energies(E_{re}) for anionic La_4^{2-} clusters.

	B3LYP			B3PW91			MP2		
	D_{4h}	C_{2v}	C_{2h}	D_{4h}	C_{2v}	C_{2h}	D_{4h}	C_{2v}	C_{2h}
R1,Å	3.270	3.072	3.055	3.241	3.140	3.106	3.341	2.241	3.210
R2,Å		3.448	3.461		3.291	3.391		3.400	3.452
A1, (°)		153.069	118.257		152.980	117.985		154.254	116.598
E_{re} ,kcal/mol	0	28.9	14.8	0	25.7	19.7	0	15.6	58.9
E_{tot} , a.u.	-124.72172	-124.67560	-124.69804	-124.85545	-124.81452	-124.82410	-123.64744	-123.62252	-123.56980

For doubly charged La_4^{2-} specie, we obtain three isomers, i.e. the square planar D_{4h} structure, the bidentate C_{2v} structure, and the open chain C_{2h} structure (Fig. 1, 1a, 1b, 1c) at the B3LYP/LANL2DZ, B3PW91/LANL2DZ and MP2/ LANL2DZ level of theory. The calculated results indicate that the square planar D_{4h} structure and the bidentate C_{2v} structure are stable on the potential energy surfaces with all real vibrational frequencies. However, another open chain C_{2h} structure is unstable because of one imaginary frequency. As seen from Table 1, the energetic stability ordering of the two stable isomers

Table 2: Optimized geometric structures and total energies (E_{tot}) for the NaLa_4^- and Na_2La_4 clusters.

	$\text{NaLa}_4^- \text{ C}_{4v}$			$\text{Na}_2\text{La}_4 \text{ D}_{4h}$		
	B3LYP	B3PW91	MP2	B3LYP	B3PW91	MP2
$\text{R}(\text{La-La}), \text{\AA}$	3.365	3.334	3.321	3.472	3.392	3.143
$\text{R}(\text{La-Na}), \text{\AA}$	3.782	3.763	4.164	3.898	3.796	3.880
$E_{tot}, \text{a.u.}$	-125.00001	-125.13762	-123.93475	-125.18519	-125.31908	-124.03815

Figure 1: Optimized geometric parameters for anion La_4^{2-} at the B3LYP level of the theory. LANL2DZ basis sets for La atoms. 6-311+G* basis sets for Na atoms.

is $1a > 1b$ at the B3LYP/LANL2DZ, B3PW91/LANL2DZ and MP2/LANL2DZ level of theory. The D_{4h} is energetically lower than the C_{2v} by 28.9, 25.7 and 15.6 kcal/mol at the above same methods. If the La_4^{2-} anion is aromatic, we should expect a special stability. Compared with the open chain C_{2h} , the D_{4h} is cyclic and is energetically lower than the C_{2h} by 14.8, 19.7 and 58.9 kcal/mol at the above same methods, denoting these species has strong stability contributing to aromaticity. Owing to the homocyclic D_{4h} structures of the La_4^{2-} , they do satisfy the first and second criteria, viz. (1) cyclic structure; (2) planarity. The La-La bond length of the square planar La_4^{2-} clusters is 3.270 Å (B3LYP/LANL2DZ), 3.241 Å (B3PW91/LANL2DZ) and 3.341 Å (MP2/LANL2DZ level). All the La-La bond lengths are shorter than the sum of covalent radii of La atom (3.38 Å), which further show the stability of the square planar structure.

Extensive searches are carried out for the NaLa_4^- and Na_2La_4 cluster using the B3LYP, B3PW91 and MP2 methods respectively. The calculated results show that pyramidal C_{4v} structures of NaLa_4^- and bi-pyramidal D_{4h} structures of Na_2La_4 are the ground state with all calculated vibrational frequencies being real using three above methods. The square planar La_4^{2-} anion is easily recognizable in the most stable C_{4v} pyramidal structures of NaLa_4^- and the most stable D_{4h} bi-pyramidal structures of Na_2La_4 which can be seen in Tables 1 and 2. The La-La bond lengths are almost identical in La_4^{2-} , NaLa_4^- and Na_2La_4 ,

showing geometrical integrity of the La_4^{2-} anion inside of the NaLa_4^- and Na_2La_4 .

The resonance energy (RE) [30] is an important energetic criterion for the aromaticity. RE (or ASE) is the extra stabilization energy relative to that of a reference structure where resonance is not present. RE has been used quite successfully for a long time in quantifying aromaticity. However, there is no common appropriate theoretical models to calculate the resonance energies for the aromatic systems to date. Several calculation schemes to estimate the resonance energies have been used, which depend strongly on the formulation of the given reaction [31]. Here, we adopt Dewar's general approach [32], which has successfully been used to estimate the RE of all-metal Al_4^{2-} cluster by [33]

$$RE(\text{La}_4^{2-}, {}^1A_{1g}) = AE(\text{La}_4^{2-} (D_{4h}, {}^1A_{1g}) \rightarrow 4\text{La}({}^2D) + e^-) - 2BE(\text{X}_2({}^1\Sigma_g) \rightarrow 2\text{La}({}^2D)) \quad (1)$$

3.2 Magnetic characteristics

The NICS values of anion La_4^{2-} are calculated at the B3LYP/LANL2DZ level of theory based on the corresponding optimized structures using the same method and are listed in Table 3. The calculated NICS values for Al_4^{2-} are also listed in Table 3 for comparison. For the square clusters Al_4^{2-} , the NICS values are computed with B3LYP/6-311+G** methods based on the corresponding optimized structures with B3LYP /6-311+G** method. The calculated NICS values show that the negative NICS values decrease in the order of NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5) and NICS(2.0) and larger than that of the clusters Al_4^{2-} respectively. Thus, it is fair to satisfy the fourth criterion.

Table 3: The calculated NICS (ppm cgsu).

	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
$\text{La}_4^{2-} (D_{4h})$	-38.21	-36.00	-30.77	-24.57	-18.65
$\text{Al}_4^{2-} (D_{4h})$	-28.48	-27.49	-24.15	-18.97	-13.64

3.3 Four-fold aromaticity

In this section, we will explore the aromaticity of all-metallic La_4^{2-} clusters by MO analysis. The valence electron configuration of Lanthanum atom is $4d^1 5s^2$. So the square clusters La_4^{2-} occupied seven valence MO orbitals: one HOMO and six energetically lower valence MOs denoted HOMO- n ($n = 1 - 6$) respectively. The HOMO-2 (e'), HOMO-3 (e') and HOMO-6 (a_1'') are completely bonding-antibonding, nonbonding, and bonding orbitals formed primarily from the filled valence s orbitals with rather small contributions from d orbitals of the component La atoms. The net bonding effect is expected to be close to zero and the s AOs can be viewed as lone pairs, because all bonding, nonbonding, and antibonding MOs composed of the same s AOs are occupied. Homo(a_1'), Homo-1(a_2'), Homo-4(a_1''), and Homo-5(a_1') are bonding orbitals mainly formed of 4d atomic orbitals (AOs) of La atoms. The Homo(a_1') orbital is delocalized bonding MO which render π

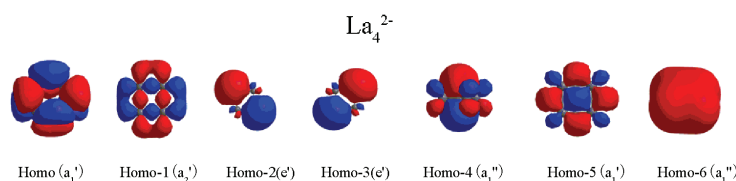


Figure 2: The occupied valence molecular orbital picture for the clusters La_4^{2-} at B3LYP/LANL2DZ level of the theory.

aromaticity. Homo-1(a_2') is represented delocalized σ Mo which oriented tangentially around the square. Clearly the Homo-4(a_1''), which is perpendicular to the plane of the square, is delocalized π Mo. Homo-5(a_1') is represented delocalized σ Mo which orients radially toward the center of the square. Therefore, the two totally delocalized σ Mos (Homo-1(a_1') and Homo-5(a_1')) in La_4^{2-} make it doubly σ -aromatic. In addition, the two totally delocalized π Mos (Homo-1(a_1') and Homo-4(a_1'')) make it doubly π -aromatic.

On the basis of the above MO analysis, the square planar La_4^{2-} ring possesses the four independent delocalized bonding systems, each with two electrons satisfying the $4n+2$ electron counting rule of aromaticity, which render these species the four-fold aromaticity.

4 Conclusions

In this paper, the equilibrium geometries, harmonic vibrational frequencies and electronic structure of the low-lying states of all-metallic anionic La_4^{2-} clusters are discussed. Comprehensive calculations show that there are two stable structure: the square planar D_{4h} structure and the bidentate C_{2v} structure respectively. The square planar D_{4h} structure is the most stable structure. The calculated NICS values indicate that a strong diatropic ring current exists in the D_{4h} square planar structure, suggesting they are highly aromatic. The detailed molecular orbital analyses confirm that all-metallic anionic La_4^{2-} clusters have the four independent delocalized bonding systems. These findings are significant for expanding the aromaticity concept into inorganic clusters La_4^{2-} .

References

- [1] P. Garratt (Wiley, New York, 1986).
- [2] V. I. Minkin, M. N. Glukhovtsev, B.Y. Simkin. (Wiley, New York, 1994).
- [3] S. Shaik, A. Shurki, D. Danovich, and P. C. Hiberty, J. Mol. Struct. (Theochem.) 155 (1997) 398.
- [4] (a) P. Schleyer and H. Jiao, Pure Appl. Chem. 68 (1996) 209; (b) P. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. Hommes, J. Am. Chem. Soc. 118 (1996) 6317.
- [5] P. Schleyer, H. Jiao, N. Hommes, V. G. Malkin, and O. L. Malkina, J. Am. Chem. Soc. 119 (1997) 12669.
- [6] P. Lazzarotti, Phys. Chem. Chem. Phys. 6 (2004) 217.

- [7] A. E. Kuznetsov, A. I. Boldyrev, X. Li, and L. S. Wang, *J. Am. Chem. Soc.* 123 (2001) 8825.
- [8] X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, L. S. Wang, *Science* 291 (2001) 859.
- [9] A. E. Kuznetsov, J. D. Corbet, L. S. Wang, and A. I. Boldyrev, *Angew. Chem. Int. Ed.* 40 (2001) 3369.
- [10] X. Li, H. F. Zhang, L. S. Wang, A. E. Kuznetsov, N. A. Cannon, and A. I. Boldyrev, *Angew. Chem. Int. Ed.* 40 (2001) 1867.
- [11] A. I. Boldyrev and A.E. Kuznetsov, *Inorg. Chem.* 41 (2002) 532.
- [12] A. E. Kuznetsov, A. I. Boldyrev, H. J. Zhai, X. Li, and L. S. Wang, *J. Am. Chem. Soc.* 124 (2002) 11791.
- [13] A. E. Kuznetsov and A. I. Boldyrev, *Struct. Chem.* 13 (2002) 141.
- [14] A. N. Alexandrova and A. I. Boldyrev, *J. Phys. Chem. A* 107 (2003) 554.
- [15] C. Mang, C. Liu, and K. Wu, *Intern. J. Quant. Chem.* 110 (2010) 1127.
- [16] J. Poater, F. Feixas, F. M. Bickelhaupt, *et al.*, *Phys. Chem. Chem. Phys.* 13 (2011) 20673.
- [17] C. Foroutan-Nejad, *Phys. Chem. Chem. Phys.* 14 (2012) 9738.
- [18] R. Islas, J. Poater, E. Matito, *et al.*, *Phys. Chem. Chem. Phys.* 14 (2012) 14850.
- [19] A. I. Boldyrev and L. S. Wang, *J. Phys. Chem. A* 105 (2001) 10759.
- [20] X. X. Chi and Y. Liu, *Int. J. Quant. Chem.* 107 (2007) 1886.
- [21] X. Huang, H. J. Zhai, B. Kiran, and L. S. Wang, *Angew. Chem. Int. Ed.* 44 (2005) 7251.
- [22] H. J. Zhai, B. B. Averkiev, D. Yu. Zubarev, L. S. Wang, and A. I. Boldyrev, *Angew. Chem. Int. Ed.* 46 (2007) 4277.
- [23] B. B. Averkiev and A. I. Boldyrev, *J. Phys. Chem. A* 111 (2007) 12864.
- [24] A. D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [25] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [26] J. P. Perdew and Y. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [27] C. Møller and M. S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [28] M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* 153 (1988) 503.
- [29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.*, *Gaussian 03W*, Revision C.02 (Gaussian, Inc., Pittsburgh, PA, 2003).
- [30] G. W. Wheland, *Resonance in Organic Chemistry* (Wiley, New York, 1955).
- [31] A. N. Alexandrova and A. I. Boldyrev, *J. Phys. Chem. A* 107 (2003) 554.
- [32] V. I. Minkin, M. N. Glukhovstev, and B. Y. Simkin, *Electronic and Structural Aspects* (Wiley, New York, 1994).
- [33] C. G. Zhan, F. Zheng, and D. A. Dixon, *J. Am. Chem. Soc.* 124 (2002) 14795.