

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

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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.

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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

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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-} ($X=B, Al, \text{ and } Ga$) 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