Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 203 (2018) 132–138

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Theoretical investigations on the *d-p* hybridized aromaticity, photoelectron spectroscopy and neutral salts of the LaX_2^- (X=Al, Ga, In) clusters

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ARTICLE INFO

Article history:
Received 29 January 2018
Received in revised form 9 May 2018
Accepted 29 May 2018
Available online 30 May 2018

Keywords:
Simulated photoelectron spectrum
Lanthanum-doped clusters
d-p hybridized aromaticity
Density functional theory
Molecular orbitals

ABSTRACT

We present an extensive density functional theory (DFT) calculations on the geometrical and electronic structures of the triatomic LaX_2^- (X=Al, Ga, In) clusters. Various trail structures and spin states have been attempted to determine the lowest-energy geometries of these La-doped metal clusters. The ground states of all three clusters are calculated to possess the trigonal structures with the singlet multiplicities. The calculations on molecular orbitals (MOs) and nucleus-independent chemical shift (NICS) values have been performed to examine the aromatic characteristics of the LaX_2^- (X=Al, Ga, In) clusters. The present calculations disclose that all these metal clusters are doubly aromatic, namely *d-p* hybridized σ and π aromaticity resulting from the effective overlap between the 5*d* atomic orbital of the La atom and the *p* orbitals of the IIIA group elements. Theoretical vertical detachment energies (VDEs) were also calculated to simulate the photoelectron spectra (PES) of the clusters. In addition, by adding the alkali cations (Li^+ and Na^+) into the LaX_2^- (X=Al, Ga, In) clusters, the geometries and electronic structures of the corresponding neutral salts have also been investigated to gain more insights in the potential of using these aromatic anions as building blocks.

1. Introduction

Almost everyone who has been exposed to the organic chemistry has learned the term "aromaticity", the concept applied to describe cyclic, planar, and conjugated molecules with delocalized π electrons and unexpected stability. The isolation of benzene was first reported by Michael Faraday in 1825, where it was found less reactive than other unsaturated hydrocarbons [1]. After that, the term "aromaticity" was introduced by Kekulé to describe a general classification of particularly stable benzene derivatives [2]. Historically, the aromatic concept has been widely used in the framework of organic chemistry, and one of the most important breakthroughs in this scientific field is that Hückel demonstrated that an aromatic closed-shell monocyclic system should have $(4n + 2)$ π electrons, namely Hückel rule [3–5]. Only recently, this important concept has been successfully advanced to the all-metal inorganic systems from the traditional organic chemistry. By employing the PES and theoretical calculations, Li et al. provided the first evidence about the existence of aromaticity in an all-metal cluster, Al_4^{2-} [6]. Subsequently, a large number of studies have been performed to explore new types of aromaticity in various inorganic metal clusters, and several comprehensive reviews have summarized the recent progresses in this interesting field [7–9].

Note that the involvement of inorganic metals in aromatic systems significantly increases the diversity of aromaticity. Compared with the traditional π-aromaticity of benzene, the participation of atomic *p* and *d* orbitals from metal atoms lead to the formation of novel σ-, π-, and δ-aromaticity in all-metal clusters [6,10–14]. Specifically, by utilizing the correlated *ab initio* and DFT methods, Kuznetsov and Boldyrev demonstrated the existence of doubly aromatic feature (σ and π) in the three-membered anionic M_3 (M=B, Al, and Ga) clusters [10]. Tsipis et al. theoretically investigated the electronic structures of cyclic hydrocoppers and proposed a *d*-orbital aromaticity [11]. By means of PES and theoretical calculations, Huang et al. provided direct experimental evidence of *d*-orbital aromaticity in the $Mo_3O_9^{2-}$ and $W_3O_9^{2-}$ clusters [12]. Additionally, the δ-aromaticity, resulting from the pure *d-d* orbital interaction, has also been observed in the $Ta_3O_3^-$ cluster by Zhai et al. [13]. Apart from the abovementioned types of aromaticity stemming from the interaction among identical atomic orbitals, a novel mode of aromaticity, namely *d-p* hybridized aromaticity, has also been observed in the La-doped boron clusters very recently [14]. This intriguing hybridized aromaticity represents a new type of bonding interaction resulting in the σ and π aromaticity.

In this work, we theoretically reported the optimized geometries and electronic structures of the three-membered LaX_2^- (X=Al, Ga, In)

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https://doi.org/10.1016/j.saa.2018.05.117
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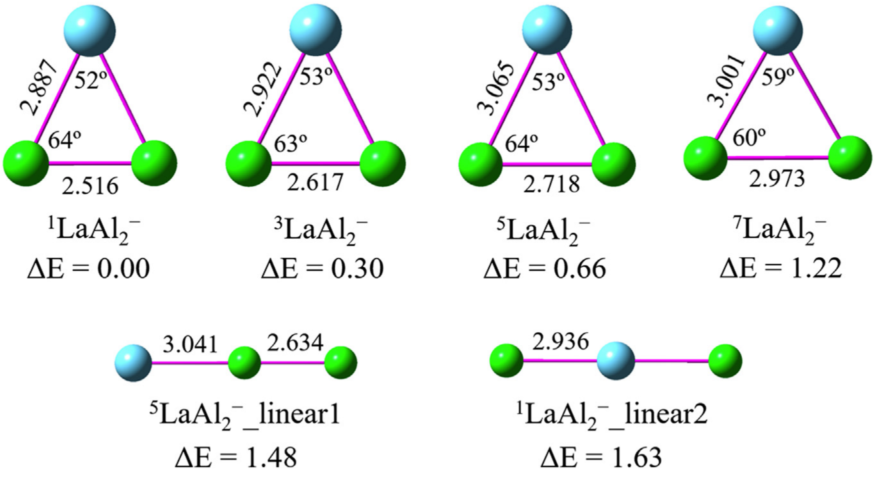

Fig. 1. The optimized lowest-energy structures and low-lying isomers of the LaAl$_2^-$ clusters calculated at the B3LYP level of theory. Bond lengths are given in angstroms (Å), and bond angles are in degrees (°). Spin multiplicity is denoted as a superscript. The relative energies ΔE with respect to the global minimum are shown in eV.

clusters. One purpose of the present study is to examine whether the *d-p* hybridized aromaticity can be preserved when isovalently substituting the non-metal boron atoms in the LaB$_2^-$ cluster by other IIIA group metal elements, namely Al, Ga, and In, respectively. By analyzing the MOs and NICS values, the LaX$_2^-$ (X=Al, Ga, In) clusters are found to be doubly aromatic, all featuring the *d-p* hybridized σ and π aromaticity. These findings provide further evidence about the existence of the hybridized aromaticity in inorganic clusters. Another objective of the current study is to predict the VDEs and simulate the PES of these clusters by employing the generalized Koopmans' theorem, which could be benefit for the assignments of the further PES experiments. It is necessary to note that, during the past several decades, there has been an extensive interest in investigating the physicochemical properties of solid LaAl$_2$ material both experimentally [15–19] and theoretically [20–22], which also motivates us to explore the properties of its corresponding sub-nano cluster. In addition, the optimized geometries and electronic structures of the corresponding neutral salts MLaX$_2$ (M=Li and Na; X=Al, Ga, In) have also been explored to show the potential of applying these anionic LaX$_2$ (X=Al, Ga, In) clusters as building blocks.

2. Computational Methods

The Gaussian 09 software package [23] was used to calculate the optimized geometries of the ground states and low-lying isomers of the LaX$_2^-$ (X=Al, Ga, In) clusters and their corresponding neutral salts MLaX$_2$ (M=Li and Na; X=Al, Ga, In). The DFT with Becke's three parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP) [24,25], which has been proven to be an accurate method to predict the geometrical, electronic structures and spectroscopic properties of small clusters recently [14,26–32], was employed here. For the lanthanum atom, its atomic orbital was described by the SDD (Stuttgart-Dresden effective core potential) with the Stuttgart-type small core (28 core electrons) and relativistic effective core potential [33–35]. Additionally, the atomic orbitals of Al, Ga, Li, and Na were represented by the augmented correlation consistent triple-zeta (aug-cc-pVTZ) basis set [36,37], while the aug-cc-pVTZ-PP small-core relativistic PP correlation consistent basis set was used for the In atom [38]. Various initial structures and spin multiplicity states have been attempted to obtain the ground states and low-lying isomers of these clusters. Full optimization was performed in the present calculations. The attainment of the energy minimum was verified by calculating the harmonic vibrational frequencies at the same level of theory, from which the zero-point energy correction was considered. Specially, in the present calculations, the zero-point energy correction has been considered in the calculations of the optimized geometries of the LaX$_2^-$ clusters and their corresponding Li and Na salts, and also the excitation energies to higher states in the PES simulation. The VDEs were calculated employing the generalized Koopmans' theorem by adding a correction term (δE) to the

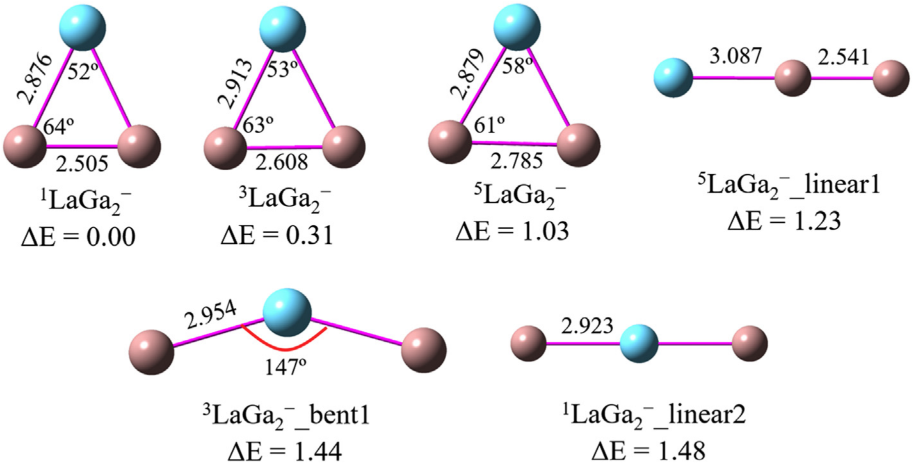

Fig. 2. The optimized lowest-energy structures and low-lying isomers of the LaGa$_2^-$ clusters calculated at the B3LYP level of theory. Bond lengths are given in angstroms (Å), and bond angles are in degrees (°). Spin multiplicity is denoted as a superscript. The relative energies ΔE with respect to the global minimum are shown in eV.