Computational and Theoretical Chemistry 1014 (2013) 8–12

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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

Density functional studies of magic clusters $Ga_{13}M(M = Li, Na, K, and Rb)$

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ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form 21 March 2013
Accepted 21 March 2013
Available online 29 March 2013

Keywords:
Ga_{13}
$Ga_{13}M(M = Li, Na, K, and Rb)$
Magic cluster
Density functional

ABSTRACT

Density functional studies are performed on the structures, stabilities, electronic properties, and polarizabilities of the $Ga_{13}M(M = Li, Na, K, and Rb)$ clusters, which have closed electronic shell structures, enhanced stabilities, large HOMO–LUMO energy gaps, high vertical ionization potentials, and low vertical electron affinities. All of these properties are characteristic of a magic cluster and can be well understood by the jellium model. Therefore, we strongly suggest $Ga_{13}M(M = Li, Na, K, and Rb)$ are magic clusters and promising as building blocks in developing cluster-assembled materials. The calculated vertical electron affinity of Ga_{13} is close to that of bromine, implying it would be like a halogen atom in the $Ga_{13}M$ molecule. The static linear polarizabilities and first-order hyperpolarizabilities of $Ga_{13}M$ clusters are significantly larger than those of Ga_{13} because of their lower symmetries and higher delocalization of p electrons.

1. Introduction

The structural stabilities of atomic clusters have been widely studied in the last decades. The cluster-assembled materials show unique properties and potential technological applications, since their physical and chemical properties are very different from those of their bulk phases [1]. A stable cluster will maintain its integrity when making cluster-based materials. One of the most fascinating developments in cluster science is the discovery of magic clusters and the subsequent explanations of magic numbers in terms of the jellium model [2], which predicts that clusters with particular numbers of valence electrons will show enhanced stabilities against dissociations due to the closed shell electronic structures. These clusters are termed as magic clusters.

The III-group atoms have three electrons in the outermost electronic shell, indicating they should be trivalent and their 13-atom clusters should have 39 valence electrons. For example, a pure Al_{13} cluster is a 39-electron system, short of just one electron to form a closed shell electronic structure, while the Al_{13}^- anion is a magic cluster with pronounced stability arising from the closed shell electronic structure [2–4]. Furthermore, when an Al atom at the center of the Al_{13} cage was replaced by a tetravalent atom such as Si, the closed shell electronic structure was realized [5–7]. Similarly, by adding an alkali atom to Al_{13}, the $Al_{13}M(M = \text{alkali atom})$ clusters will contain 40 valence electrons and closed shell electronic structures. Over the past years, numerous theoretical investigations have predicted that $Al_{13}M(M = Li–Cs)$ were stable molecules consisting of an anionic core of Al_{13}^- cage and an M^+ cation located on the outer surface [7–12], indicating they could be building blocks for cluster-based materials. For instance, the experimental mass spectra and anion photoelectron spectroscopies of $Al_nM(M = Li, K, and Cs)$ clusters [10,12,13] have shown their enhanced abundances in mass spectra and reduced vertical electron affinities (VEAs) versus cluster size trend, making them stepping stones toward forming ionic cluster-assembled materials. Following, Liu et al. [14] have found $In_{13}M(M = Li, Na, and K)$ were magic clusters with strong stabilities.

As composed of the III-group atoms, Ga_n clusters have shown interesting properties. For example, Weiß et al. [15] have observed maximum abundances of Ga_{13}^- and $Ga_{12}Si^-$ anions in the experimental mass spectra, and have discovered that both Ga_{13}^- and $Ga_{12}Si^-$ anions should be decahedron (D_{5h}) symmetric. Guo [16] has calculated that $Ga_{13}Al$ was more stable than the neighboring $Ga_nAl(n = 1–15)$ clusters. Yuan et al. [17] have found $Ga_{12}X(X = C, Si, Ge, Sn, and Pb)$ were magic clusters.

However, studies are limited to the magic Ga_nM clusters up to now. The Ga_{13} cluster with 39 valence electrons left an interesting research to explore the electronic structure. One way is to adsorb a one-electron atom, thus the new cluster will have 40 valence electrons and gain electronic stability by closing the $1s^21p^61d^{10}2s^21f^{14}2p^6$ electronic shell. To our knowledge, no systematic theoretical investigations on alkali atom doped gallium clusters have been reported. In this work, we will present systematic density functional studies of the $Ga_{13}M(M = Li, Na, K, and Rb)$ clusters, and aim to answer the following questions: (1) What are the lowest-energy structures of the $Ga_{13}M(M = Li, Na, K, and Rb)$ clusters? (2) Whether the $Ga_{13}M$ clusters are magic? In what follows, we will first describe the computational details, then present our results and discussion, and end with our final conclusion.

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http://dx.doi.org/10.1016/j.comptc.2013.03.024

2. Computational details

The calculations in this paper are carried out by Dmol^3 package [18]. Generalized gradient approximation (GGA) [19] based on density functional theory (DFT) [20] is adopted. The Becke–Lee–Yang–Parr (BLYP) correlation exchange functional, a combination of the Becke exchange functional [21] and the Lee–Yang–Parr (LYP) correlation functional [22], is adopted. The used basis sets are double-numerical quality basis sets with polarization functions (DNP), comparable to Gaussian 6-31G** basis sets. Electronic structure is obtained by solving the spin-polarized Kohn–Sham (KS) equations self-consistently. The convergence thresholds are set to 0.002 Hartree for the force, 0.005 Å for the displacement, and 10^{-5} Hartree for the energy change. Self-consistent field calculations are carried out with a convergence criterion of 10^{-6} Hartree on the total energies. Mulliken population analyses are made to obtain the effective charge and net spin population on each atom. The stabilities of the optimized geometries are confirmed by vibrational frequency analyses. Therefore, all isomers we identified for each cluster are surely local minima, and the optimized structures include possible Jahn–Teller distortions.

The accuracy of the current computational scheme is tested by the calculation of the Ga_2 dimer. We obtain a length (2.49 Å) of Ga–Ga bond that fits well with the theoretical value of 2.46 Å [23] and the experimental Ga–Ga bond distance of 2.57 Å in the a-gallium crystal [24]. The vibrational frequency (237.5 cm^{-1}) of Ga_2 is in good agreement with the previous theoretical value of 208.3 cm^{-1} [23]. The vertical electron potential (VIP) (1.27 eV) of Ga_2 agrees well with the experimental value of 1.60 eV [25]. Therefore, our approach provides an efficient way to study the $Ga_{13}M$(M = Li, Na, K, and Rb) clusters.

The finite field (FF) method was applied to investigating the polarizabilities of molecules [26–28]. When a molecule is subjected to an electronic field (F), the energy (E) of a molecule can be in Taylor series as expressed in the equation [29]:

$$E = E^{(0)} - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_K - \dots\dots\dots \quad (1)$$

where $E^{(0)}$ is the energy of molecule in the absence of an electronic field, μ_i is the component of the dipole moment vector, α_{ij} is the static linear polarizability tensor, β_{ijk} is the first-order hyperpolarizability tensor, i, j and k are the designated different components in the x, y, and z directions respectively. The molecular Hamiltonian includes a term $(-\mu_0.\bar{F})$ describing the interaction between the external uniform static field and the molecule. μ_0 is the molecular total dipole moment. A set of equations are given through calculating the energy with each electric field, and then the μ_i, α_{ij}, and β_{ijk} values can be obtained through simultaneous equations by altering E with respect to F.

An appropriate electric field has significant effect on the polarizabilities and hyperpolarizabilities. Two different and opposite requirements governing the choice of an electric field should be satisfied at the same time. First, the field must be large enough to ensure that the imprecision in the calculated dipole moments is small when compared with the contribution to the dipole moment expansion. Second, the field must be small enough so that the error incurred by the truncation of the expansion is acceptable. In our calculations, an external electric field of 0.001 a.u. is added to the molecules along x, y, and z directions. Apart from the tensor components of the static linear polarizabilities, we also consider the mean static dipole polarizability $\langle\alpha\rangle$, the anisotropy $\Delta\alpha$ of the static linear polarizability tensor which can be used as a measure of the anisotropy of the cluster's electron density, and the first-order hyperpolarizability β_0. These quantities are defined as [30,31]:

$$\langle\alpha\rangle = [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]/3 \quad (2)$$

$$\Delta\alpha = \sqrt{[(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{xx}-\alpha_{zz})^2 + (\alpha_{yy}-\alpha_{zz})^2]/2} \quad (3)$$

$$\beta_0 = \frac{3}{5}(\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z)/\mu_0 \quad (4)$$

where

$$\beta_i = \beta_{ixx} + \beta_{iyy} + \beta_{izz} \quad (i = x, y, z) \quad (5)$$

Our aim is not only to verify whether the DFT provide a qualitative representation about the static linear polatizabilities and first-order hyperpolarizabilities of these systems, but also to test their abilities in offering utilizable static linear polatizabilities and first-order hyperpolarizabilities for successful quantitative predictions.

3. Results and discussion

3.1. Structures and stabilities

The selection of initial geometries is important to the reliabilities of the obtained ground-state structures. Many possible isomers have been reported for the 13-atom clusters, such as, two geometries with I_h and O_h symmetries have been considered as the starting configurations of Al_{13} and In_{13} clusters [8,14]. Four isomers with I_h, D_{5h}, C_{5v}, and C_s symmetries have been optimized for the $Ga_{12}X$(X = C, Si, Ge, Sn, and Pb) clusters [17], however, the C_{5v} structure is formed by adsorbing the tetravalent atom on the vertex of the D_{5h} structure of Ga_{12}, thus, the D_{5h} and C_{5v} symmetric structures are the same for Ga_{13}. Therefore, four probable geometries with O_h, I_h, C_s and D_{5h} symmetries are taken as the initial isomers for Ga_{13} in this paper, as shown in Fig. 1a. The O_h structure is a cuboctahedron, a compact portion of the fcc crystal lattice. The D_{5h} structure can be obtained from the I_h one by rotating the top pentagonal cap by 36°.

The calculated binding energies(BEs) are −24.47 eV, −22.50 eV, −23.44 eV, and −25.75 eV respectively for the O_h, I_h, C_s and D_{5h} symmetric structures, therefore, the D_{5h} isomer should be the most stable structure, as same as that reported for Ga_{13} [15], In_{13} [14], and Al_{13} [8]. The initial geometries of $Ga_{13}M$(M = Li, Na, K, and Rb) are all generated from the D_{5h} symmetric Ga_{13}. The M atom which occupies a top, a bridge, or a hollow site in the initial structures of $Ga_{13}M$ shifts to the hollow site after optimization, suggesting that the hollow site shown in Fig. 1b should be the most stable for M, similar to those for M in both $Al_{13}M$(M = Li, Na, and K) [8] and $In_{13}M$(M = Li, Na, and K) [14]. Furthermore, the lowest-energy structures obtained for $Ga_{13}M$(M = Li, Na, K, and Rb) clusters are quite similar and are all C_{2v} symmetric.

Table 1 presents the adsorption energies (E_{ad}s) and energy gaps (E_gs) of Ga_{13} and $Ga_{13}M$(M = Li, Na, K, and Rb). The E_{ad} of $Ga_{13}M$ can be calculated according to $E_{ad} = E(Ga_{13}) + E(M) - E(Ga_{13}M)$. If the E_{ad} is greater than zero, it means the reaction is exothermic [32]. A larger E_{ad} value indicates a higher stability. In our calculation, all $Ga_{13}M$ clusters have the positive E_{ad}s, which are remarkably larger than that of the $Ga_{13}Al$ [16], therefore, four $Ga_{13}M$(M = Li, Na, K, and Rb) clusters are rather stable and the reactions to synthesize them should be exothermic and favorable.

Additionally, we compare the E_gs shown in Table 1. The E_g, defined as the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), is another useful quantity for examining the kinetic stability of a cluster [33]. A larger E_g corresponds to a higher strength required to perturb the electronic structure. Our calculated E_gs of $Ga_{13}M$ indicate that the M adsorption can remarkably enhance the kinetic stabilities of the structures.