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Structures of small Y*n*Al*m* clusters ($n + m \leqslant 6$): A DFT study

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ABSTRACT

We conducted DFT studies on the Y*n*Al*m* binary clusters of size $n + m \leqslant 6$, to study electronic property variation, using the PBE1PBE method and Lanl2DZ as basis set. The ground-state geometries of yttrium ($n \geqslant 4$) prefer 3D geometry and Al ($m \leqslant 5$) desires planar geometry. Yttrium clusters were stabilized by the addition of one or two aluminum atoms. The shape and geometry of the clusters has a profound influence on their band gap and stability. With an increase in the Al composition, segregation was found to occur in the bimetallic systems with the geometry and shape depending on the aluminum composition. The bimetallic clusters have higher electron affinity and stability.

1. Introduction

Studies on bimetallic clusters have received great attention owing to their chemical and physical properties, which can be tuned by varying the composition, atomic ordering, and size of the clusters [1]. Their surface structures, compositions, and segregation properties are of interest; moreover, these studies have been important in determining chemical reactivity which has led to widespread applications in electronics, engineering and catalysis [2]. Though large advances have been made in experimental physics to produce size-selected clusters, they lack the ability to directly explore and assign cluster geometries and discriminate between possible isomers. Of particular interest are aluminum alloys which are light weight, high strength, and corrosion resistance. Hence much research has been carried out to study the bimetallic clusters of aluminum [3–5]. Studies on the substitution of the transition metal show that they increase the stability of the materials. However, theoretical studies of such clusters have faced difficulties due to the presence of *d* electrons, with complicated electronic ground-states structure with different spin multiplicities [6].

Yttrium shows great promise as a catalyst [7]. Yttrium in its composites such as Yttrium Aluminum Granite (YAG), finds applications in optical sensors with high sensitivity or in X-ray detection material [8]. Moreover, yttrium can be added to reduce the grain size in chromium, molybdenum, zirconium, and titanium, and to increase the strength of aluminum and magnesium alloys [9]. Besides, yttrium alloys are extensively used in bulk metallic glasses [10]. Aluminum and its alloy clusters were found be capable of acting as reversible hydrogen storage materials [11]. Only recently, attention has been paid to the structure and stability of monometallic yttrium clusters by using the DFT method [12,13]. In a recent study, Yuan et al. reported on the structure and electronic properties of small yttrium clusters of size $n = 2$–17 and observed that the growth evaluation favors 3D clusters formation with a oscillatory behavior in their HOMO–LUMO gap. On the contrary, much attention was paid to *ab initio* and density functional modeling of aluminum clusters [14–18]. Ahlrichs and Elliot investigated the structure stability of aluminum clusters and observed that the 2D planar configurations were of the lowest energy for clusters of $m = 5$. The nature of the heterometallic bond has been extensively studied using experimental and theoretical methods [19,20]. Theoretical investigations have been done on $CuAl^-$ clusters [21], Al–Ti clusters [3], Al–Ni clusters [4], Al–B clusters [22], Al–Si clusters [5], and Al–Fe clusters [23].

With the view to understanding the structure, stability and properties, of the type Y*n*Al*m* ($m + n \leqslant 6$), we have made a theoretical investigation on the small bimetallic clusters over the complete composition range from pure yttrium to pure aluminum cluster. We present the results obtained for various YAl clusters according to the composition of the clusters and have compared their properties with monometallic clusters.

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2. Computational method

All the calculations have been performed by means of different combinations of exchange and correlation terms as implemented in the Gaussian package [24]. We have compared the effect of various methods, on the experimental results available for the Al_2 and Y_2 clusters with the theoretical results (Table 1) with various forms of exchange-correlation functional, denoted as BP86, B3LYP, B1LYP, BPW91, mPWP86, B3PW91, BPBE, PBEPBE, PBE1PBE, and SVWN, using the valence basis sets LANL2DZ. Local spin density approximation method predicts shorter bond lengths and higher frequency, ionization potential (IP) and binding energy (BE) for Al_2 and Y_2 clusters. Methods using hybrid exchange functional underestimate frequency for Al and Y dimer. A comparison with the experimental results shows that PBE1PBE is the most optimal method. PBE1PBE is the generalized-gradient-approximation (GGA) exchange-correlation functionals of Perdew et al. [25,26]. The basis set LANL2DZ which uses relativistic effective core potential basis set of double-ζ quality was used as recent results on the transition metal clusters reveal that the relativistic effective core potentials (RECPs) treatment is essential to get a high level of accuracy [27].

The structures are optimized with various spin multiplicity, and the one which has the global minima were shown in Table 2. The binding energy/atom (BE/atom) to identify the most stable cluster is calculated from

$$\mathrm{BE/atom} = \frac{nE(\mathrm{Y}) + mE(\mathrm{Al}) - E(\mathrm{Y}n\mathrm{Al}m)}{n+m} \qquad (1)$$

where $E(\mathrm{Y})$, $E(\mathrm{Al})$, and $E(\mathrm{Y}n\mathrm{Al}m)$ are the total energies of the Y atom, Al atom and Y*n*Al*m* cluster. The common HOMO–LUMO gap (E_G) is computed as the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital and is provided in Table 3. The vertical ionization potential (VIP) and electron affinity (EA) were calculated as shown below.

$$\mathrm{VIP} = E[\mathrm{Y}n\mathrm{Al}m]^{+} - E[\mathrm{Y}n\mathrm{Al}m]$$

$$\mathrm{VEA} = E[\mathrm{Y}n\mathrm{Al}m] - E[\mathrm{Y}n\mathrm{Al}m]^{-}$$

where $n = 1–5$ and $m = 5–X$; $E[\mathrm{Y}n\mathrm{Al}m]^{+}$ is the energy of the cation; $E[\mathrm{Y}n\mathrm{Al}m]^{-}$ is the energy of the anion and $E[\mathrm{Y}n\mathrm{Al}m]$ is the energy of the neutral cluster.

3. Computational results

The optimized geometries of the Y*n*Al*m* ($n + m \leqslant 6$) clusters are discussed according to their composition and the number of atoms Fig. 1. For the monometallic and bimetallic clusters, the optimized bond lengths, their ground-state spin multiplicity (M) and structural symmetries are shown in Table 2. Their BE/atom, HOMO–LUMO band gap (E_G), ionization potential (IP), electron affinity (EA), and vibrational frequency are provided in Table 3. To assess the accuracy of our calculations, we have compared some properties of the clusters with available experimental values as shown in Tables 1–3 and the results are presented according to cluster dimension.

3.1. Geometry

3.1.1. YnAlm (n + m = 2)

Concurrent with the experimental and recent theoretical studies on yttrium and aluminum, our findings on Y_2 and Al_2 clusters show that the ground-state spin multiplicity are quintet and triplet, respectively. The calculated bond length of Al_2 $R_0 = 2.833$ Å is comparable with the experimental value of $R_0 = 2.701$ Å. The theoretical BE value for Al_2 dimer is 1.34 eV which is very close to the experimental value of 1.37 eV predicted by resonant two-photon ionization spectroscopy on the jet-cooled Al_2 molecule [28]. Moreover the harmonic frequency and the ionization potential calculated by the present method was 250.7 cm^{-1} and 6.20 eV, which are close to the experimental values of 284.2 cm^{-1} [29] and 6.20 eV [30], respectively. Pettersson et al. [14] predicted a bond length of 2.751 Å using correlated wave functions and extended basis sets. Jones [15] reported a value of 2.717 Å using a pseudopotential basis set. In a recent work, Rao and Jena [17] calculated the bond length to be 2.860 Å using BPW91 method and with a LanL2DZ basis set.

The available experimental results for the Y_2 cluster are the vibrational frequency and ionization potential whose values were 194 cm^{-1} [31] and 4.96 eV [32]. The present calculations show very close values of 185 cm^{-1} and 5.04 eV as vibrational frequency and ionization potential, respectively. The bond length calculated by us was 2.915 Å whose values are in close agreement with the recent results [12]. The BE values predicted by us was

Table 1

The calculated binding energy BE (eV), bond distance R_0 (Å), vibrational frequencies (cm^{-1}) and ionization potential (eV) for Al_2 and Y dimer in different DFT methods with LANL2DZ basis sets.

Method	Al_2				Y_2			
	BE (eV)	R_0 (Å)	ω (cm^{-1})	IP (eV)	BE (eV)	R_0 (Å)	ω (cm^{-1})	IP (eV)
SVWN	1.69	2.573	314.7	7.13	2.55	2.892	193.7	5.72
BLYP	1.25	2.884	220.6	5.95	1.39	2.959	179.9	4.98
B1LYP	1.13	2.854	235.7	5.93	0.921	2.933	189.4	4.91
B3LYP	1.19	2.854	235.1	6.09	1.11	2.932	188.9	5.07
BP86	1.43	2.867	231.9	6.29	1.80	2.936	184.7	5.29
mPWP86	1.47	2.867	232.1	6.30	1.85	2.933	185.3	5.31
B3P86	1.36	2.833	246.4	6.74	1.57	2.907	193.4	5.66
BPW91	1.43	2.857	236.2	6.24	1.83	2.938	184.8	5.13
B3PW91	1.33	2.838	245.9	6.24	1.51	2.920	191.8	5.01
BPBE	1.44	2.857	236.7	6.23	1.84	2.937	185.2	5.11
PBEPBE	1.51	2.857	238.1	6.23	1.90	2.935	186.1	5.12
PBE1PBE	1.37	2.833	250.7	6.20	1.49	2.915	194.0	5.04
Expt.	1.34 ± 0.06[a]	2.701 ± 0.00[a]	284.2[b]	6.20[c]	–	–	185[d]	4.96 ± 0.05[e]

[a] See Ref. [28].

[b] See Ref. [29].

[c] See Ref. [30].

[d] See Ref. [31].

[e] See Ref. [32].