IJST (2015) 39A4: 485-489
Iranian Journal of Science & Technology

http://ijsts.shirazu.ac.ir

First principles study of H_2O and NH_3 adsorption on the pristine and B-doped $Al_{12}N_{12}$ nanocluster

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Abstract

Adsorption of NH_3 and H_2O molecules on pristine and B–doped $Al_{12}N_{12}$ nano–cage was investigated using density functional theory, by means of B3LYP and X3LYP functionals. Both NH_3 and H_2O molecules were found to bind to an Al atom of $Al_{12}N_{12}$ via chemisorption, releasing energies ranging from –1.48 to –1.53 and –1.16 to –1.22 eV, respectively. The binding energies of X3LYP functional are somewhat larger than those of the B3LYP. The Morokuma–Kitaura energy decomposition approach reveals that the nature of these interactions is mainly electrostatic rather than covalent. The $Al_{12}N_{12}$ strongly adsorbs these molecules without any change in its electronic properties namely, these processes are *electronically ineffectual*. B–doping decreases the adsorption energies of the studied molecules whereas it cannot affect the sensitivity of the $Al_{12}N_{12}$ towards them.

Keywords*:* Aluminum nitride nanocluster; adsorption; theoretical study; DFT

1. Introduction

Nanomaterials have attracted great interest in recent years because of their excellent mechanical, electrical, electronic, optical, magnetic and surface properties. Since the discovery of C_{60} (Kroto et al., 1985), several studies on different nanostructures, such as fullerene–like clusters, nanotubes, nanocapsules, nanopolyhedra, cones, cubes and onions have been reported (Iijima, 1991; Novoselov et al., 2004; Beheshtian et al., 2012). Interest in fullerene valence isoelectronic clusters especially III–V clusters, is also growing rapidly and has become routine in the literature. As an example, aluminum nitride (AlN) has attracted interest for its possible applications in optoelectronics, high–temperature electronics, acousto–electronics and as anti–wear coatings. Accordingly, Al_nN_n structures have been widely studied both theoretically and experimentally (Belbruno et al., 1999; Guo et al., 2005; Guo et al., 2004).

It has been confirmed experimentally that the electronic properties of nanostructured materials such as carbon nanotubes can be appreciably altered by the presence of adsorbates (Collins et al., 2000). Gas adsorption on nanoclusters is a great issue for both essential research and applied application of these materials. The adsorptive characteristics of nanostructured materials in the gas phase resulted in their use as gas sensors of pollutant gases, storage of fuels, and removal of hazardous pollutants from gas streams (Peng and Cho, 2003). Many different aspects of nanotube and nanocluster interactions with adsorbates have been explored experimentally and computational studies (Chen et al., 2001).

Over the past decade, nanotube functionalization has been extensively studied (Baierle et al., 2007), while the functionalization of nanoclusters has remained unexplored. Recently, Wang *et al.* (2009) investigated the capability of AlN nanostructures (nanocages, nanocones, nanotubes, and nanowires) to store hydrogen using gradient–corrected density functional theory (DFT). They have shown that the AlN nanostructures may be appropriate materials for hydrogen storage.

Here, we report a theoretical study on the adsorption of NH_3 and H_2O on an AlN nanocluster of $Al_{12}N_{12}$. In this work, computations based on DFT calculations were performed to elucidate the effects of these molecules on electronic and structural properties of the cluster.

2. Computational methods

Geometry optimizations were performed on the all studied systems using two density functionals (B3LYP and X3LYP) combined with 6–31G* basis sets as implemented in GAMESS suite of program (Schmidt et al., 1993). The B3LYP is a commonly used approach in the studies of nanostructured

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Received: 18 April 2014 / Accepted: 3 January 2015

materials (Ahmadi et al., 2011; Khaybullin et al., 2011; Beheshtian et al., 2011). However, it fails in the calculation of noncovalant interactions, that is, we once more used the X3LYP functional (Hoe et al., 2001) to compare the results. All energy calculations, molecular electrostatic potential surfaces (MEP), natural bond orbital (NBO) and density of states (DOS) analyses were done using the same functional with 6–311+G* basis sets. We define the adsorption energy (E_{ad}) of adsorbates as follows:

$$E_{ad}=E(\text{adsorbate}/Al_{12}N_{12})–E(Al_{12}N_{12})–E(\text{adsorbate}),$$

where E(adsorbate /$Al_{12}N_{12}$) is the total energy of an adsorbate molecule combined with the $Al_{12}N_{12}$, and E ($Al_{12}N_{12}$) and E (adsorbate) are the total energies of the $Al_{12}N_{12}$ and an adsorbate (NH_3 or H_2O) molecule, respectively. By definition, a negative value of E_{ad} corresponds to exothermic adsorption.

3. Results and discussion

3.1. *H_2O and NH_3 adsorption on pristine $Al_{12}N_{12}$*

Optimized structure of $Al_{12}N_{12}$ is built from six squares and eight hexagons (Fig. 1a). Structurally, there are two individual Al–N bond types among the 36 Al–N bonds in the $Al_{12}N_{12}$; one is shared by two six–membered rings (B_{66}), and another by a four–and a six–membered ring (B_{64}). The calculated DOS at X3LYP level for the $Al_{12}N_{12}$ nano–cage is shown in Fig 1b with HOMO–LUMO gap (E_g) of 3.98 eV.

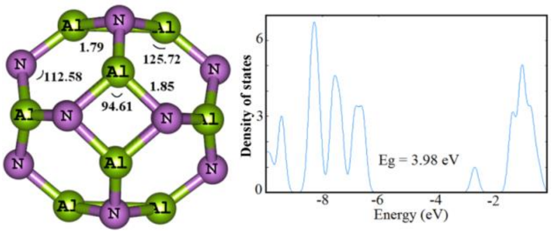

Fig. 1. (a) Geometrical parameters of an $Al_{12}N_{12}$ nanocluster (b) the electronic density of state (DOS) for the $Al_{12}N_{12}$ cluster. Bond lengths are in Å and angles in degree. The results are obtained using X3LYP functional

In order to determine the most favorable adsorption site for NH_3 on the exterior surface of the $Al_{12}N_{12}$ cluster, a number of distinct starting structures were used; for example, the nitrogen atom of ammonia was put atop a hexagonal or square ring; the nitrogen atom was put close to the B atom of cluster; and hydrogen atoms were located on the top of three N atoms of cluster.

Table 1. Calculated Equilibrium cluster-molecule distance (D) and adsorption energies (E_{ad}) of H_2O and NH_3 adsorbed on the $Al_{12}N_{12}$ nanocluster

Method	molecule	^{a}*D* (Å)	$^bE_{ad}$ (eV)
X3LYP	NH_3	2.03	-1.53
	H_2O	1.96	-1.22
B3LYP	NH_3	2.04	-1.48
	H_2O	1.98	-1.16

Based on our fully relaxed X3LYP geometry, we obtained only one stable final adsorbed form of NH_3/cluster in which the N atom of the NH_3 is close to the Al atom of the cluster with a distance of 2.03 Å, and a large E_{ad} of –1.53 eV (Table 1). The result of our B3LYP optimized geometry is somewhat similar to those of the X3LYP, so that the X3LYP shows a slightly stronger adsorption. The adsorption of the NH_3 on the Al site in target cluster can be explained by the fact that, in the $Al_{12}N_{12}$, the Al atoms are electron poor sites and also the LUMO of the cluster is rather more localized at these sites, therefore, the Al atoms are strong Lewis acids and force an NH_3 molecule to share additional electron with them.

A local structural deformation at the adsorption site of cluster can be observed upon the NH_3 molecule adsorption. The bond length of B_{66} and B_{64} of cluster is increased from 1.79 and 1.85 Å in the pristine $Al_{12}N_{12}$ to 1.82 and 1.89 Å in the adsorbed form (Fig. 2a), respectively. As shown in Table 2, the E_g of the cluster has no significant change after adsorption of NH_3 on the cluster. This phenomenon may be related to the nature of this interaction which will be discussed in a forthcoming section. It is noteworthy to mention that only the results of X3LYP functional were reported in Figs. 1 and 2. However, the results of the B3LYP are somewhat similar to those of the X3LYP.

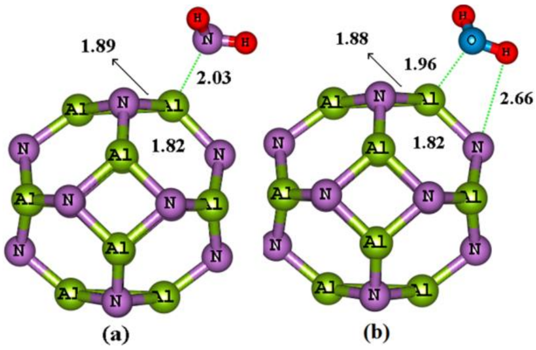

Fig. 2. Optimized structures of NH_3 (a) and H_2O (b) chemisorption on an $Al_{12}N_{12}$ cluster. The distances are in Å

Subsequently, taking the $Al_{12}N_{12}$ as an adsorbent, various possible adsorption geometries of the water molecule were investigated; the O or H atom of

H_2O is close to either the Al atom or the N atom of the cluster. As shown in Fig. 2b, one stable adsorption state was found in which an oxygen atom of H_2O is close to an Al atom of the cluster. The calculated E_{ad} and the binding distance (defined as the length between the adsorbed N atom of the cluster and the O atom of molecule) are summarized in Table 1. Based on the X3LYP calculations, the most stable configuration has an E_{ad} of –1.22 eV, slightly lower than that of the NH_3 adsorption, and the interaction distance of O–Al is 1.96 Å.

Table 2. HOMO, LUMO energies (eV), and HOMO–LUMO energy gap (E_g, eV) calculated for pristine and adsorbate/$Al_{12}N_{12}$ complex

System	HOMO	LUMO	E_g
Pristine	-6.57	-2.59	3.98
NH_3	-6.08	-2.26	3.82
H_2O	-6.17	-2.16	4.01

Moreover, H_2O adsorption induces a structural deformation to both the H_2O molecule and the $Al_{12}N_{12}$. The H_2O adsorbed Al atom is pulled outward from the cluster wall with the bond lengths increasing from 1.79 and 1.85 Å in the pristine cluster to 1.82 and 1.88 Å in the H_2O/cluster complex (see the Figs. 1 and 2). The NBO analysis shows that such structural deformation results in the change of adsorbing Al atom hybridization from sp^2 to sp^3. The deformation of the system structure and the appreciable E_{ad} suggests that this interaction is chemisorption.

Table 3. Percentage of electrostatic (E_{ES}), exchange (E_{EX}), and polarization (E_{PL}) energies obtained from attractive interaction energy decomposition based on Morokuma-Kitaura approach.

Energy	NH_3	H_2O
E_{ES}	68.3	63.4
E_{EX}	25.3	26.8
E_{PL}	6.4	9.4

Similar to the NH_3 adsorption, here, the adsorbing Al atom acts as a Lewis acid, forcing the H_2O molecule to share an additional electron with them. In addition, the E_g value of cluster is changed from 3.98 to 4.01 eV upon the H_2O adsorption. Therefore, it is concluded that like the NH_3 adsorption, the H_2O adsorption process does not significantly affect the electrical conductivity of the $Al_{12}N_{12}$ cluster, and the adsorption can be called *electronically harmless modification*.

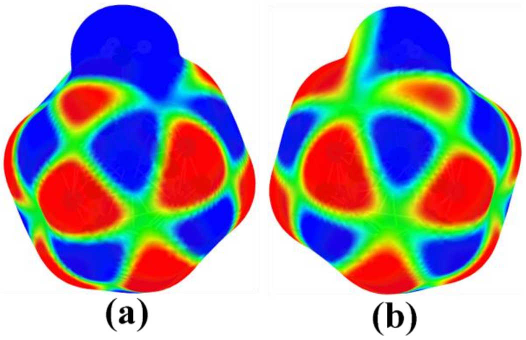

Fig. 3. Calculated molecular electrostatic potential surfaces for (a) NH_3 and (b) H_2O adsorbed on the $Al_{12}N_{12}$. The surfaces are defined by the 0.0004 electrons/b^3 contour of the electronic density. Color ranges, in a.u.: blue, more positive than 0.020; red, more negative than –0.020

The calculated MEP plots in Fig. 3, show the charge distribution on the H_2O– and NH_3–cluster complexes. The blue color on both adsorbates indicates that the cluster acts as an electron acceptor. The interaction energies of NH_3 or H_2O with the $Al_{12}N_{12}$ complexes have been analyzed using the Morokuma–Kitaura (MK) energy decomposition method, and the nature of the adsorption has been investigated. The MK approach is based on the recalculation of the supermolecule's SCF energy lacking specific elements of the Fock and overlap matrices which can be associated to the energy terms. The decomposed interaction energy between two fragments A and B takes the following form: $\Delta E^{SCF} = E_{PL} + E_{ES} + E_{CT} + E_{EX} + E_{MIX}$, where E_{PL} is the polarization energy, E_{ES} is the electrostatic term, taking into account the Coulombic interactions between the unperturbed charge distribution of A and B. Physically, the E_{ES} includes all the permanent charges and multipole interactions. The E_{EX} is the exchange repulsion, *i.e.* the short–range repulsion caused by the overlap of the electron distribution of A and B, the E_{CT} is the charge transfer term, *i.e.* basically the interaction which originates from the charge transfer from occupied molecular orbitals of A to empty molecular orbitals of B and vice versa. The E_{MIX} term accounts for the coupling between all the above terms, it is simply evaluated by the difference between the SCF energy and the summation of the E_{ES}, E_{PL}, E_{EX} and E_{CT} contributions.

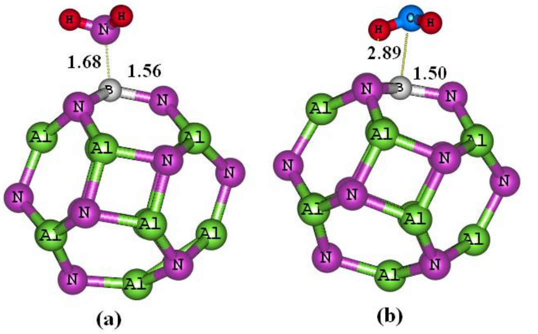

Fig. 4. Optimized structures of NH_3 (a) and H_2O (b) chemisorption on a B–doped cluster. The distances are in Å

Here, we focused on the three attractive terms E_{ES}, E_{PL} and E_{CT}. The calculated percentages of these terms are collected in Table 1, indicating that the electrostatic force is the basic factor of attractive interaction between either the NH_3 or H_2O and the $Al_{12}N_{12}$. According to the MK analysis they provide 68.3% and 63.4% of attractive interaction, respectively. Charge transfer energies make little contribution to the E_{ad} of both molecules. Thus, despite the large amount of E_{ad}, the E_g does not change significantly (Table 2). We think that the electrostatic nature of this interaction is the reason why these molecules cannot affect the electronic properties of cluster. As known these properties are affected by large charge transfers between the adsorbates and adsorbents. As shown in Table 3, here, the E_{CT} is very small and negligible term.

The findings are very similar to our previous study on the NH_3 interaction with AlNNTs (Ahmadi et al., 2011). We have shown that despite the strong interaction, the chemical modification of AlNNTs with the NH_3 leads to a slight change in the electronic properties of AlNNTs and the nature of this interaction is mainly electrostatic rather than covalent. It seems that this trend may be a characteristic property of AlN nanostructures due to their polar surface bonds with high ionicity. However, more investigations (on different gas adsorptions) are needed to obtain a general conclusion.

3.2. H_2O and NH_3 adsorption on B–doped $Al_{12}N_{12}$

We attempted to find the effects of B doping on the H_2O and NH_3 adsorption behavior of $Al_{12}N_{12}$. By replacing an Al atom with B (B_{Al}), the geometric structure of the cluster is dramatically distorted. The calculated bond lengths of B–Al are 1.45 and 1.51 Å, also E_g of cluster was slightly decreased from 3.98 to 3.78 (5% change) after boron doping in $Al_{12}N_{12}$ cluster. Optimized structures of the adsorbate/B–doped cluster complexes are shown in Fig. 4. The E_{ad} were calculated to be –0.25 and –0.86 eV and the adsorption distance is 2.89 and 1.68 Å for H_2O and NH_3 adsorption, respectively, based on the X3LYP method. Compared with the pristine cluster, in the B–doped $Al_{12}N_{12}$ the E_{ad} of H_2O and NH_3 on the similar site is decreased (Table 4).

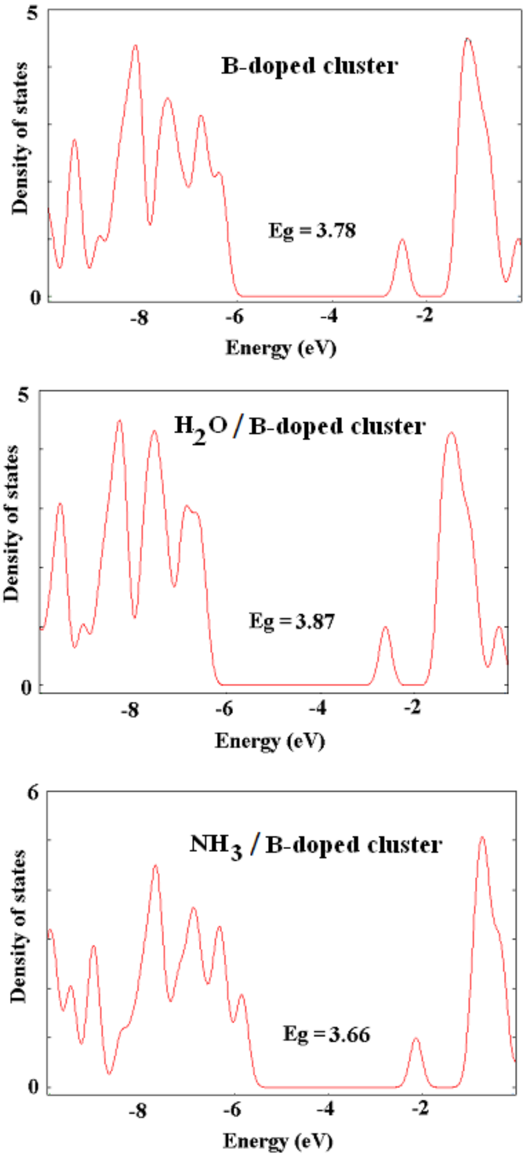

Fig. 5. Calculated density of states (DOS) for doped cluster

Table 4. Calculated Equilibrium cluster-molecule distance (D) and adsorption energies (E_{ad}) of H_2O and NH_3 adsorbed on the B-doped nanocluster

Method	molecule	^{a}D (Å)	$^{b}E_{ad}$ (eV)
X3LYP	NH_3	1.68	-0.86
	H_2O	2.89	-0.25
B3LYP	NH_3	1.71	-0.81
	H_2O	2.94	-0.20

To examine the sensitivity of $Al_{12}N_{12}$ to H_2O and NH_3 molecules, we calculated the DOS of the most stable combined systems of gas/$BAl_{11}N_{12}$ and compared them with that of the free B–doped cluster. It can be found that for gas/$BAl_{11}N_{12}$ complex the DOS near the Fermi level is not affected by the gas adsorption. On the other hand, after adsorption of H_2O and NH_3 on cluster, the E_g of the cluster shows no significant change.

4. Conclusions

We have studied the adsorption of H_2O and NH_3 molecules on the surface of pristine and B–doped $Al_{12}N_{12}$ nanocluster, by means of B3LYP and X3LYP density functionals. It was found that the molecules can be adsorbed on the cluster surface by attaching to an Al atom with adsorption energies in the range of –1.16 to –1.53 eV. The Morokuma–Kitaura energy decomposition approach demonstrated that the nature interactions are mostly electrostatic rather than sole covalent. We showed that B–doping in the surface of cluster dramatically decreases the adsorption energies without significant changes on the electronic structure.

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