First principles study of H₂O and NH₃ adsorption on the pristine and B-doped Al₁₂N₁₂ nanocluster

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Abstract

Adsorption of NH₃ and H₂O molecules on pristine and B–doped Al₁₂N₁₂ nano–cage was investigated using density functional theory, by means of B3LYP and X3LYP functionals. Both NH₃ and H₂O molecules were found to bind to an Al atom of Al₁₂N₁₂ 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 Al₁₂N₁₂ 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 Al₁₂N₁₂ 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 C₆₀ (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; Beheshitian 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, AlₙNₙ 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 NH₃ and H₂O on an AlN nanocluster of Al₁₂N₁₂. 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
materials (Ahmadi et al., 2011; Khaybullin et al., 2011; Beheshtian et al., 2011). However, it fails in the calculation of noncovalent 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:

\[ E_{ad} = E(\text{adsorbate}/\text{Al}_{12}\text{N}_{12}) - E(\text{Al}_{12}\text{N}_{12}) - E(\text{adsorbate}) \]

where \( E(\text{adsorbate}/\text{Al}_{12}\text{N}_{12}) \) is the total energy of an adsorbate molecule combined with the \( \text{Al}_{12}\text{N}_{12} \), and \( E(\text{Al}_{12}\text{N}_{12}) \) and \( E(\text{adsorbate}) \) are the total energies of the \( \text{Al}_{12}\text{N}_{12} \) and an adsorbate (\( \text{NH}_3 \) or H2O) molecule, respectively. By definition, a negative value of \( E_{ad} \) corresponds to exothermic adsorption.

3. Results and discussion

3.1. H2O and NH3 adsorption on pristine \( \text{Al}_{12}\text{N}_{12} \)

Optimized structure of \( \text{Al}_{12}\text{N}_{12} \) 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 \( \text{Al}_{12}\text{N}_{12} \): 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 \( \text{Al}_{12}\text{N}_{12} \) nano–cage is shown in Fig 1b with HOMO–LUMO gap (\( E_g \)) of 3.98 eV.

![Fig. 1. (a) Geometrical parameters of an \( \text{Al}_{12}\text{N}_{12} \) nanocluster (b) the electronic density of state (DOS) for the \( \text{Al}_{12}\text{N}_{12} \) cluster. Bond lengths are in Å and angles in degree. The results are obtained using X3LYP functional](image)

In order to determine the most favorable adsorption site for \( \text{NH}_3 \) on the exterior surface of the \( \text{Al}_{12}\text{N}_{12} \) 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.

![Fig. 2. Optimized structures of \( \text{NH}_3 \) (a) and H2O (b) chemisorption on an \( \text{Al}_{12}\text{N}_{12} \) cluster. The distances are in Å](image)

Subsequently, taking the \( \text{Al}_{12}\text{N}_{12} \) as an adsorbent, various possible adsorption geometries of the water molecule were investigated; the O or H atom of

<table>
<thead>
<tr>
<th>Method</th>
<th>molecule</th>
<th>( D ) (Å)</th>
<th>( E_{ad} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X3LYP</td>
<td>( \text{NH}_3 )</td>
<td>2.03</td>
<td>-1.53</td>
</tr>
<tr>
<td></td>
<td>H2O</td>
<td>1.96</td>
<td>-1.22</td>
</tr>
<tr>
<td>B3LYP</td>
<td>( \text{NH}_3 )</td>
<td>2.04</td>
<td>-1.48</td>
</tr>
<tr>
<td></td>
<td>H2O</td>
<td>1.98</td>
<td>-1.16</td>
</tr>
</tbody>
</table>

Table 1. Calculated Equilibrium cluster-molecule distance (\( D \)) and adsorption energies (\( E_{ad} \)) of H2O and \( \text{NH}_3 \) adsorbed on the \( \text{Al}_{12}\text{N}_{12} \) nanocluster

Based on our fully relaxed X3LYP geometry, we obtained only one stable final adsorbed form of \( \text{NH}_3 \)/cluster in which the N atom of the \( \text{NH}_3 \) 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 \( \text{NH}_3 \) on the Al site in target cluster can be explained by the fact that, in the \( \text{Al}_{12}\text{N}_{12} \), 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 \( \text{NH}_3 \) molecule to share additional electron with them.

A local structural deformation at the adsorption site of cluster can be observed upon the \( \text{NH}_3 \) 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 \( \text{Al}_{12}\text{N}_{12} \) 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 \( \text{NH}_3 \) 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.
H₂O is close to either the Al atom or the N atom of the cluster. As shown in Fig. 2h, one stable adsorption state was found in which an oxygen atom of H₂O 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 NH₃ adsorption, and the interaction distance of O–Al is 1.96 Å.

### Table 2. HOMO, LUMO energies (eV), and HOMO–LUMO energy gap (E₆, eV) calculated for pristine and adsorbate/Al₁₂N₁₂ complex

<table>
<thead>
<tr>
<th>System</th>
<th>HOMO</th>
<th>LUMO</th>
<th>E₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>-6.57</td>
<td>-2.59</td>
<td>3.98</td>
</tr>
<tr>
<td>NH₃</td>
<td>-6.08</td>
<td>-2.26</td>
<td>3.82</td>
</tr>
<tr>
<td>H₂O</td>
<td>-6.17</td>
<td>-2.16</td>
<td>4.01</td>
</tr>
</tbody>
</table>

Moreover, H₂O adsorption induces a structural deformation to both the H₂O molecule and the Al₁₂N₁₂. The H₂O 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 H₂O/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 sp² to sp³. 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.

<table>
<thead>
<tr>
<th>Energy</th>
<th>NH₃</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_ES</td>
<td>68.3</td>
<td>63.4</td>
</tr>
<tr>
<td>E_EX</td>
<td>25.3</td>
<td>26.8</td>
</tr>
<tr>
<td>E_PL</td>
<td>6.4</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Similar to the NH₃ adsorption, here, the adsorbing Al atom acts as a Lewis acid, forcing the H₂O molecule to share an additional electron with them. In addition, the E₆ value of cluster is changed from 3.98 to 4.01 eV upon the H₂O adsorption. Therefore, it is concluded that like the NH₃ adsorption, the H₂O adsorption process does not significantly affect the electrical conductivity of the Al₁₂N₁₂ cluster, and the adsorption can be called electronically harmless modification.

Fig. 3. Calculated molecular electrostatic potential surfaces for (a) NH₃ and (b) H₂O adsorbed on the Al₁₂N₁₂. The surfaces are defined by the 0.0004 electrons/b³ 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 H₂O– and NH₃–cluster complexes. The blue color on both adsorbates indicates that the cluster acts as an electron acceptor. The interaction energies of NH₃ or H₂O with the Al₁₂N₁₂ 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: \( \Delta E_{SCF} = E_{PL} + E_{ES} + E_{EX} + E_{MX} \), 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. Physicscaly, 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_MX 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.
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$_2$O 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 $E_d$ 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$_2$O and NH$_3$ adsorption on B–doped Al$_{12}$N$_{12}$

We attempted to find the effects of B doping on the H$_2$O 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 $E_d$ 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$_2$O 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$_2$O and NH$_3$ on the similar site is decreased (Table 4).

![Fig. 4. Optimized structures of NH$_3$ (a) and H$_2$O (b) chemisorption on a B–doped cluster. The distances are in Å](image)

![Fig. 5. Calculated density of states (DOS) for doped cluster](image)

**Table 4.** Calculated Equilibrium cluster-molecule distance ($D$) and adsorption energies ($E_{ad}$) of H$_2$O and NH$_3$ adsorbed on the B-doped nanocluster

<table>
<thead>
<tr>
<th>Method</th>
<th>molecule</th>
<th>$D$ (Å)</th>
<th>$E_{ad}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X3LYP</td>
<td>NH$_3$</td>
<td>1.68</td>
<td>-0.86</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>2.89</td>
<td>-0.25</td>
</tr>
<tr>
<td>B3LYP</td>
<td>NH$_3$</td>
<td>1.71</td>
<td>-0.81</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>2.94</td>
<td>-0.20</td>
</tr>
</tbody>
</table>
To examine the sensitivity of Al$_2$N$_{12}$ to H$_2$O and NH$_3$ molecules, we calculated the DOS of the most stable combined systems of gas/BAi$_2$N$_{12}$ and compared them with that of the free B-doped cluster. It can be found that for gas/BAi$_2$N$_{12}$ complex the DOS near the Fermi level is not affected by the gas adsorption. On the other hand, after adsorption of H$_2$O and NH$_3$ on cluster, the $E_g$ of the cluster shows no significant change.

4. Conclusions

We have studied the adsorption of H$_2$O and NH$_3$ molecules on the surface of pristine and B-doped Al$_2$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.

References


