

Stability of Ga₆N₆ clusters in a nitrogen environment

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Abstract. The interaction of the ground state structure of Ga₆N₆ cluster with nitrogen is studied using an ab initio molecular orbital method. We find that the ground state isomer preferably reacts with extra nitrogen atoms nearby, transforming into other sized clusters such as Ga₆N₇ or Ga₆N₅. We conclude, therefore, that Ga₆N₆ would not be likely to survive in an atomic nitrogen environment. In addition, such structural transformation can be understood by analyzing the strength variation of related bonds arising from the adsorption of a N atom.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Jn Reactivity of clusters – 82.65.+r Surface and interface chemistry; heterogeneous catalysis at surfaces

1 Introduction

With a wide band gap in their electronic band structures, GaN crystals have become important materials in the micro-electronic and optical industries [1,2]. Besides the crystals, GaN clusters as well as their sisters, M_mN_n (M = Al or In) [3,4], have been paid increasing attention with the aim of improving device preparation processes. Experimentally, various GaN clusters have been produced through laser-ablated gallium atoms reacting with nitrogen atoms and molecules [5]. Apart from pure GaN clusters, some GaN cluster-based isomers were investigated [6–8]. For example, Ga₃N₃H₁₂ and Ga₄N₄H₁₈ clusters exhibiting nonlinear optical properties were found. Thus GaN cluster-based materials have potential applications in efficient photonic systems [6]. On the theoretical side, Kandalam et al. [3,4,9,10] studied the structures and electronic properties of neutral and charged nonstoichiometric M_mN_n ($m, n = 1, 2$; M = Al, Ga and In) clusters as well as stoichiometric (MN)_n ($n = 3–6$; M = Al, Ga and In) clusters based on density functional theory (DFT) within the non-local density approximation. They suggested that the lowest energy structure of the Ga₆N₆ cluster is a planar configuration.

It is worth noting that in the process of preparing GaN clusters there are abundant N atoms and N₂ molecules surrounding the generated GaN clusters. This raises the question of whether or not these N atoms and N₂ molecules will react with the GaN clusters, which have been regarded as stable to date? If such reactions occur, those so-called

stable GaN clusters will be unstable in such a nitrogen environment. This would then raise another question: what is the mechanism for chemical etching of the clusters in the nitrogen environment?

In this paper, the interaction between a Ga₆N₆ cluster and an additional nitrogen atom is studied. We find that it is easy for nitrogen atoms to react with the ground state structure of the Ga₆N₆ cluster, but difficult for nitrogen molecules. So, our calculations demonstrate that the Ga₆N₆ cluster might be etched by atomic nitrogen. The mechanism of such etching is discussed by analyzing related natural bond orbitals (NBOs) in the concerned systems.

2 Computational methods

We employ the Gaussian 98 quantum chemistry package [12] at the B3LYP/6-31G(d) level of density functional theory to calculate the interaction between the Ga₆N₆ cluster and a N atom or a N₂ molecule. The exchange-correlation functional and the basis set we choose above are suitable for dealing with our concerned systems according to previous theoretical studies [4,11,13,14]. In our calculations, spin polarization terms are included for the systems containing odd electrons.

3 Interaction between the Ga₆N₆ cluster and an extra nitrogen atom

The ground state structure of the Ga₆N₆ cluster is taken from reference [3]. After full relaxation of this isomer

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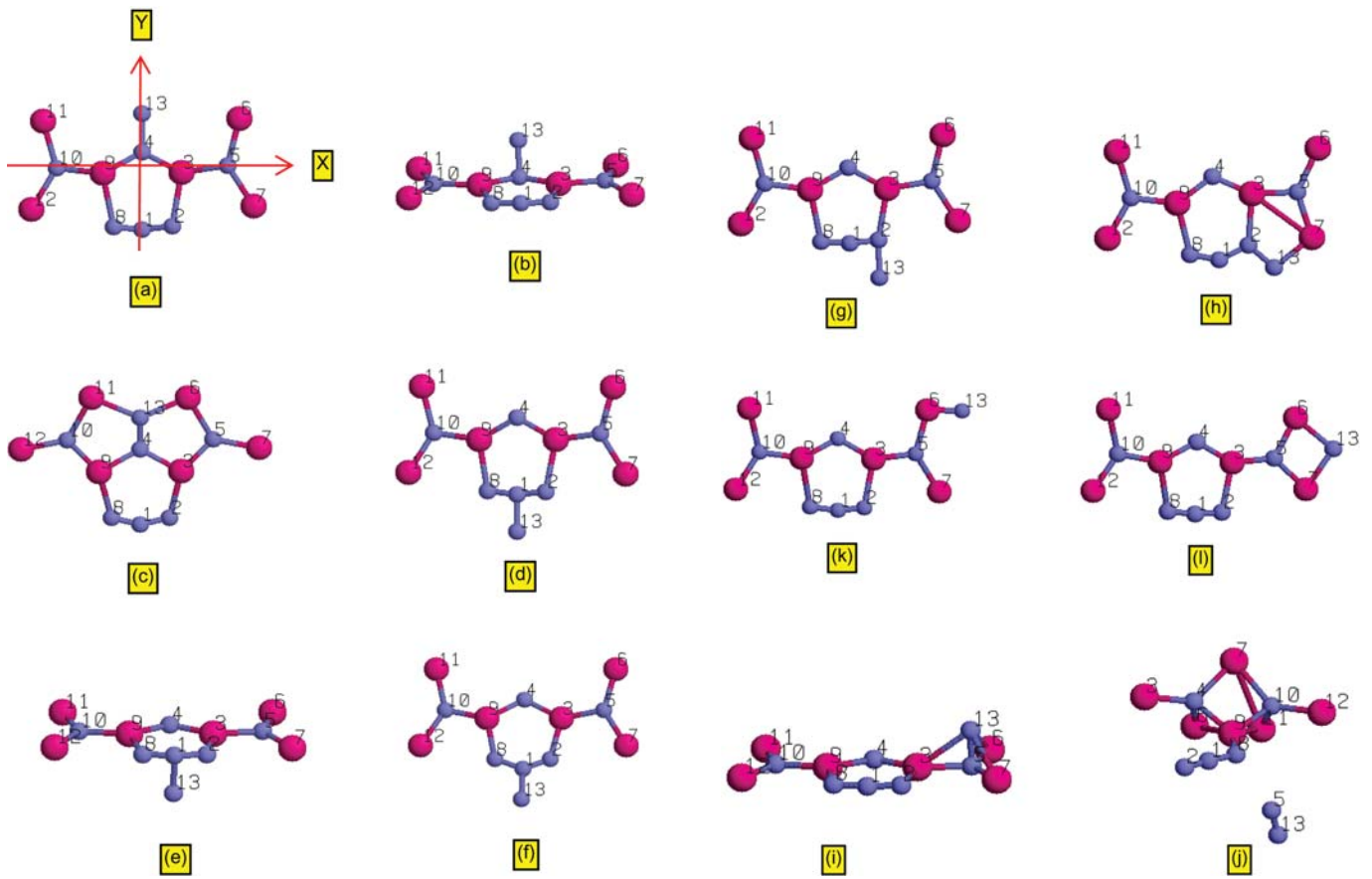


Fig. 1. (Color online) The adsorption of N(13) on concerned sites in the ground state structure of the Ga_6N_6 cluster. Big balls (red) represent Ga atoms, and small balls (blue) represent nitrogen atoms.

using the Gaussian 98 package as mentioned above, we find that the resulting structure of this isomer is in excellent agreement with that reported in reference [3], except for a very small discrepancy (no more than 1.5%) in the bond lengths. Such agreement again supports the assertion that our calculations at the level of B3LYP/6-31G(d) for the current systems are reliable. Since N atoms are more reactive than N_2 molecules, we first examine the interaction of an extra N atom with the ground state Ga_6N_6 cluster. Two kinds of adsorption paths are considered here: the extra nitrogen atom of N(13) approaching the N(4) in the cluster either in the y -direction (Fig. 1a) [15] or within the yz -plane (Fig. 1b) with a spacing of about 1.5 Å. We find that this extra N atom can automatically adsorb on the N(4) atom, without overcoming any energy barrier in these adsorption processes. Interestingly, the resulting configurations (Fig. 1c) obtained via the two different pathways are exactly the same. This implies that the adsorption of an extra nitrogen on the N(4) atom in the cluster not only happens very easily, but is not so sensitive to the adsorption pathway.

Next, we investigate the interaction of the extra N atom, N(13), with the existing N_3 subunit in the ground state Ga_6N_6 cluster. There are three different cases considered for the adsorption of N(13) on the N_3 subunit:

N(13) adsorbing on N(1) in either y -direction (Fig. 1d) or z -direction (Fig. 1e), or N(13) adsorbing on N(2) in y -direction (Fig. 1g). In the cases of (d) and (e), the relaxed structure of the N_4 subunit exhibits a ‘Y’ type configuration (Fig. 1f). When the N(13) atom bonds with either N(2) or N(8) (Fig. 1g), the subsequent N_4 subunit in the derivative cluster of Ga_6N_7 shows a zigzag structure locally (Fig. 1h).

In addition, interactions between the extra N atom and the Ga atom (Ga(6)) and the threefold coordinated nitrogen atom (N(5)) in the cluster are also taken into account, shown in Figures 1i and 1k. For the case (k), as the N(13) adsorbing on Ga(6) in the x -direction, this external N atom equidistantly bonds with Ga(6) and Ga(7) with bond lengths of 2.1 Å in the optimal configuration (Fig. 1l). In the case (i), the extra N atom connects with N(5), forming a N_2 subunit with a strong N–N bond. This N_2 subunit does not bond with its neighbouring Ga atoms effectively, resulting in dissociation of this N_2 subunit from the system and the formation of a Ga_6N_5 cluster which is of three-dimensional shape (Fig. 1j).

In summary, owing to the adsorption of an extra N atom, the initial Ga_6N_6 cluster may change into Ga_6N_7 or Ga_6N_5 . Energetically, the resulting structure of case (c) is more stable than the other cases for Ga_6N_7 clusters.

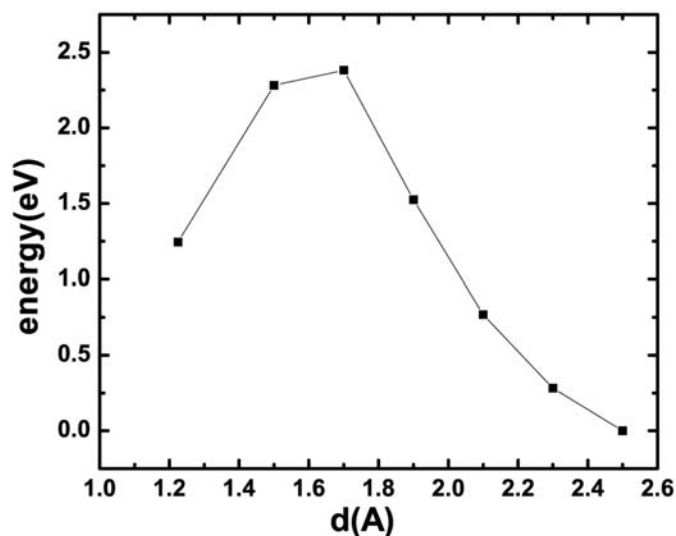


Fig. 2. (Color online) The adsorption energy of a N₂ molecule versus the distance between N(4) and its nearest N atom in the N₂. The step-size is 0.2 Å. The total energy of the initial configuration where there is no interaction between the N₂ and the cluster is taken as a reference.

This does not mean that the structure of the Ga₆N₇ cluster in case (c) is the ground state isomer, but only implies that an extra N atom favourably adsorbs on the N(4) in the lowest energy isomer of the Ga₆N₆ cluster, leading to the ground state structure of the Ga₆N₇ cluster. All of these calculations strongly demonstrate that the lowest energy isomer of the Ga₆N₆ cluster does not survive well under the atmosphere of N atoms.

4 Interaction between Ga₆N₆ and a nitrogen molecule

As well as N atoms, N₂ molecules are also contained in a nitrogen environment. Hence, it is important for us to investigate the interaction of a N₂ molecule with the lowest energy isomer of the Ga₆N₆ cluster. Since the N(4) atom is more reactive than the other atoms in the cluster, we only consider the adsorption of a N₂ molecule on the N(4). In our calculations, the system of Ga₆N₆ + N₂, in which the distance between N(4) in the cluster and N(13) in the N₂ is initially set to be 2.5 Å, is fully optimized. We observed that the N₂ molecule does not adsorb on the N(4) in the cluster automatically even though the N(4) atom is reactive. This means that there probably exists an energy barrier to hinder the adsorption of a N₂ molecule. To evaluate the energy barrier, we bring the N₂ molecule towards the N(4) atom along the *y*-direction step by step, with a step-size of 0.2 Å. At each step, the entire system is fully relaxed while fixing the coordinates of the N(4) in the cluster and the N(13) atom in the N₂ molecule. When the distance between N(4) and N(13) is 1.5 Å, the whole system is fully relaxed with removing the constraints applied above, and the N₂ molecule spontaneously adsorbs

Table 1. The calculated Wiberg bond index for the isolated Ga₆N₆ cluster and three configurations shown in Figure 3.

bond	isolated	(a)	(b)	(c)
1–2	1.9082	1.8167	1.6781	1.7061
2–3	0.3264	0.4297	0.5851	0.5638
2–8	0.6614	0.5613	0.4085	0.4364
3–4	1.0336	0.5358	0.4947	0.4540
3–5	0.7622	0.7800	0.8147	0.8484
5–6	0.4532	0.4695	0.4267	0.4287
5–7	0.4443	0.4196	0.4453	0.4567
4–13		1.1225	1.4759	1.3990
6–13		0.0093	0.0475	0.3336
11–13		0.0093	0.0481	0.3246

on the N(4). From this calculation, we obtain the energy barrier of the N₂ adsorption to be about 2.5 eV, as shown in Figure 2. This energy barrier, caused by the interaction between the triple bond of the N₂ molecule and the σ orbital in the N(4) atom, predominantly involves stretching and weakening the N–N bond in the N₂ molecule. Clearly, such a high energy barrier almost rules out the possibility of a N₂ molecule adsorbing on the Ga₆N₆ cluster.

5 Discussion

The structural transition of the Ga₆N₆ cluster caused by the adsorption of an extra N atom will be reflected in the electronic structures of the considered systems. The bonding character of a bond in a cluster can be measured by the Wiberg bond index (WBI) [16] that is obtained from NBO calculations. According to the definition of the WBI, the values of the WBI being one, two and three correspond respectively to the perfect single, double and triple covalent bond, and the value of the WBI is zero for a noncovalent bond [17]. Hence, the larger the value of the WBI, the stronger the covalent bond between the two atoms.

Table 1 lists the calculated WBI of the isolated Ga₆N₆ cluster. For the isolated Ga₆N₆ cluster, we find that the WBI of two N–N bonds are 1.91, being much larger than those of all the Ga–N bonds which are in the range 0.32–1.04. So, the N–N bonds are stronger than the other bonds in the Ga₆N₆ cluster. In addition, the strength of a N–Ga bond depends on its local bonding environment: if the Ga and N atoms that surround a N–Ga bond arrange alternately, and if the N atom and Ga atom in this N–Ga bond are twofold coordinated and threefold coordinated respectively, this N–Ga bond is the most stable. Whereas the strength of a Ga–N bond consisting of a threefold coordinated N atom and a singly coordinated Ga atom is the weakest. The others, such as the Ga(3)–N(5) bond, are between the two extreme cases.

Next, we focus on the adsorption of an extra N atom on the Ga₆N₆ cluster. According to the results obtained above, we know that the extra N atom adsorbs preferably on the twofold coordinated N atom, N(4). Therefore, we

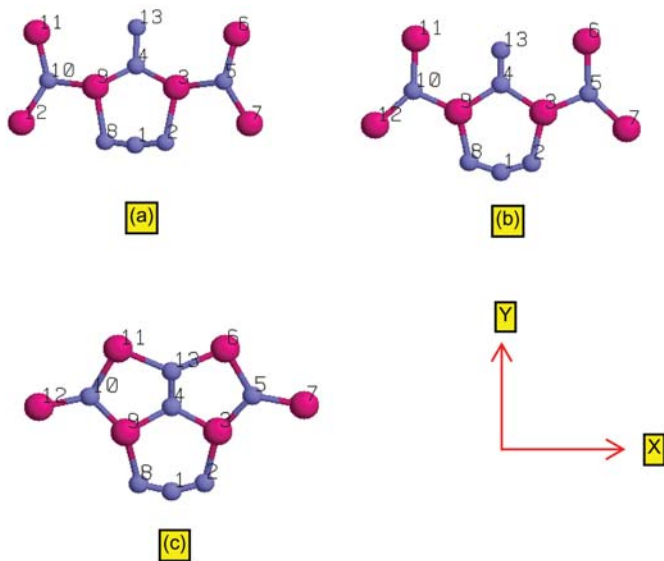


Fig. 3. (Color online) Three snapshots taken from the process of an extra atom adsorbing on the N(4) in the ground state structure of a Ga_6N_6 cluster; (a) is the initial structure with the distance of 1.5 Å between N(13) and N(4); (b) an intermediate structure with the N(13)–N(4) distance of 1.2 Å, and (c) is the final structure. Big balls (red) represent Ga atoms, and small balls (blue) represent nitrogen atoms.

only consider the case that the extra N atom adsorbs on the N(4) atom. For this adsorption process, three snapshots, such as the initial, an intermediate and the final structures, are plotted in Figure 3. From Figure 3, we find that the extra N atom N(13) takes the lead in adsorbing on the N(4) and then bonds to two Ga atoms, Ga(6) and Ga(11), forming a threefold coordinated configuration at atom N(13) finally. Such a structural transformation is essentially associated with the variations in the related WBI of the system, as listed in Table 1.

Table 1 also tells us that, as the extra N atom approaches the N(4) in the cluster gradually, the WBI values of three bonds, N(4)–N(13), N(13)–G(6) and N(13)–Ga(11), become larger and larger apparently. In the meantime, both N(4)–Ga(3) and N(4)–Ga(9) bonds are weakened. The values of WBI for other bonds in the system are not perturbed significantly. In fact, when N(13) connects with N(4), some electron charge on Ga(3) and Ga(9) transfer to the N(13)–N(4) subunit, leading to changes in the electronic structure of the system. On the other hand, although N(13) preferably connects with the N(4) in the initial stage of the adsorption process, it still interacts with Ga(6) and Ga(11) weakly, which can be reflected by the WBI values listed in Table 1. Such a weak interaction together with the changes of the electron distribution in the system drives both Ga(3)–N(5) and Ga(9)–N(10) to rotate around Ga(3) and Ga(9) within the xy -plane, respectively. As a result, N(13) tightly bonds with N(4), Ga(6) and Ga(11), forming the final structure shown in Figure 3c.

In the case of an extra N atom reacting with N(5) (seen in Fig. 1k), the calculated WBI values (Tab. 2) clearly

Table 2. The calculated Wiberg bond index for the adsorption of an extra N atom on N(5) in the Ga_6N_6 cluster shown in Figure 1k.

bond	WBI	bond	WBI
1–2	2.2823	6–9	0.2185
1–8	1.5775	6–11	0.7333
2–3	0.0084	7–10	0.2481
2–8	0.6383	7–11	0.1324
3–4	0.3694	8–9	0.5558
3–5	0.0003	9–10	0.5176
4–6	0.4120	9–11	0.2058
4–7	0.2491	10–11	0.3983
4–9	0.5108	10–12	0.3681
5–6	0.0033	3–13	0.0002
5–7	0.0029	5–13	3.0063
6–7	0.1262	7–13	0.0018

indicate that the adsorption of N(13) on N(5) forms a strong N–N bond and weakens the N(5)–Ga(i) ($i = 3, 6, 7$) bonds heavily, indicating that both N(13) and N(5) almost do not bond with their neighbouring atoms. Thus, the N(13)–N(5) subunit takes off from the cluster, leaving a Ga_6N_5 cluster behind.

6 Summary

In conclusion, through calculating the adsorption behaviour of either an extra N atom or a N_2 molecule on several sites in the ground state structure of the Ga_6N_6 cluster, we find that the ground state Ga_6N_6 cluster can easily react with an extra N atom but only with difficulty with a N_2 molecule. Furthermore, it is revealed that, with the adsorption of an extra N atom, the Ga_6N_6 cluster transforms into a Ga_6N_7 cluster or a Ga_6N_5 cluster. Therefore, our results demonstrate that the ground state structure of the Ga_6N_6 cluster could not stably exist in an atomic nitrogen environment. Moreover, the NBO analysis shows that the adsorption of an extra N atom make the electrons redistribute in the system, driving the transformation of cluster structures.

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