A computational study on structure and stability of nitrogen-doped titanium clusters Ti_nN (n = 1-10)

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Abstract

A study was performed using density functional theory at the PW91PW91/DGDZVP2 level to investigate the structures and stability of the neutral nitrogen-doped titanium clusters Ti_nN (n = 1-10). The most stable isomers may have spin state ranging from doublet to quartet to sextet. Interestingly, the ground-state structures of these clusters are consistently formed by adding an N atom on an edge and a face of the pure titanium cluster and the N atom prefers to stay on surface of the clusters. Doping with an N atom increases the stability of titanium clusters and decreases their metallicity. Moreover, the analyses of average binding energy, second-order energy differences and fragmentation energy according to cluster size imply a special stability of Ti_6N.

Keywords. N-doped titanium clusters, PW91PW91 functional, cluster stability, electronic structure, HOMO-LUMO gap.

1. INTRODUCTION

Cluster is a type of nanoscale materials, often possesses novel physical, chemical properties and is expected to have various valuable applications in science and daily life. During the past several decades, the studies of atomic cluster, particularly transition metal clusters, have been developed with interesting discoveries on geometrical structures and magnetic properties. In addition, doping other elements into a host cluster brings in interesting characteristics. Studies of pure and doped transition metal clusters provide an opportunity to understand structural patterns to build bulk materials from atoms, as well as chemical and physical properties of clusters in different sizes.

Up to date the main interest has been focused on clusters of the late transition metals, such as Ni, Cu, Au, Ag, Pt, Pd… [1,2] while much less attention to clusters of the early transition metals such as Sc, Ti, and V. Recently, some effort has been devoted to pure and doped Ti clusters to explore their geometrical and electronic structures both experimentally and theoretically, for example Ti_nAl [3], $Ti_{12}Fe$, $Ti_{12}C$, $Ti_{12}N$, $Ti_{12}P$ [5], Ti_nNi [5] etc.

It was shown that non-metallic dopants have a good potential to change stability and properties of the pure Ti clusters [4, 6]. For example, the P-doping increases stability and changes magnetic properties of the pure Ti_n cluster [6]; and $Ti_{12}P$ has much higher HOMO–LUMO gap than Ti_{13} cluster [4]. To the best of our knowledge, a systematic theoretical and experimental research in small Ti clusters doped with nitrogen atom has not been available yet. Therefore, this work aims to study geometrical structures, stability and electronic properties of Ti_nN clusters (n=1-10) by utilizing Density Functional Theory (DFT) in order to understand the effects of the nitrogen atom to small titanium clusters.

2. COMPUTATIONAL METHODS

All calculations were performed within the density functional theory with the generalized gradient approximation using Gaussian 03 package (Revision E.01) [7]. The DFT-PW91PW91 method, in which both the exchange and correlation functionals were developed by Perdew and Wang in 1991 [8], was applied to optimize structures, calculate harmonic frequencies and analyze electronic properties. Such an approach was successfully employed to study the titanium cluster in the previous works [9-11]. The double-zeta DGDZVP2 basis set [12] which is augmented with the polarization functions was applied for all the calculations.

In the search of isomers for Ti_nN clusters, we considered various positions of the N atom in the

molecular structure to explore as many as possible isomers of the cluster and then identify the low-energy isomers for the further analysis.

3. RESULTS AND DISCUSSION

3.1. Geometrical structures of Ti_nN

We have found many structural isomers for the Ti_nN (n = 1-10) clusters. Numbers of isomers rapidly increase with the number of atoms in the clusters. Among them, a few lower-lying isomers are selected to show in Fig. 1 for detailed discussion. The global minimum of each Ti_nN cluster is determined by comparing the total energies (corrected by Zero-Point Energy) of the low-lying isomers. The isomers are labelled as $TinN$-x, where n is number of Ti atoms, x = a, b, c, ... is labelled for the isomer with increasing energy. Point group, electronic state and relative energy (in eV) of the isomers compared to the lowest-energy one of a given cluster are provided together with their structures. Shapes of the lowest-lying isomers of the pure titanium clusters (shown in figure 2) are taken from previous studies [13-15] and re-optimized using the same level of theory in the present work to compare with the doped clusters.

The dimer TiN is stable at the possibly lowest spin state of $^2\Sigma^-$. The lowest energy isomer of trimer Ti_2N is an N-centered isosceles trigonal with C_{2v} symmetry (**Ti2N-a**). This isomer is stable at quartet spin state $^4B_1$. Additionally, two linear structures (not shown in Fig. 1) are found to be much higher in energy than the **Ti2N-a**-quartet (0.65 and 3.01 eV, respectively).

For n = 3, the three-dimensional structure (**Ti3N-b**) in doublet spin state ($^2A'$) appears to be a stable structure but less stable than the planar one (**Ti3N-a**) in quartet spin state ($^4B_1$). The doublet state of the planar structure **Ti3N-a** lies 0.30 eV higher in energy than the corresponding quartet state.

For n = 4, three structural isomers are found for this size. The **Ti4N-a** and **Ti4N-b** are formed by substituting a Ti atom in the triangular bipyramid Ti_5 by an N atom at axial and horizontal positions, respectively. The **Ti4N-c** is formed by adding an N atom to the tetrahedron Ti_4. The **Ti4N-a** is most stable at the quartet spin state while the **Ti4N-b** and **Ti4N-c** are stable at the lower-spin $^2B_1$ and $^2B_2$, respectively.

The low-energy isomers of Ti_5N are closely related to the triangular bipyramidal shapes of Ti_5 cluster. **Ti5N-a** and **Ti5N-b** isomers have low-spin states of $^2A''$ and $^2B_2$, respectively. The **Ti5N-c** is at

higher spin state $^4A''$ and 0.63 higher in relative energy to the lowest-energy isomer **Ti5N-a**.
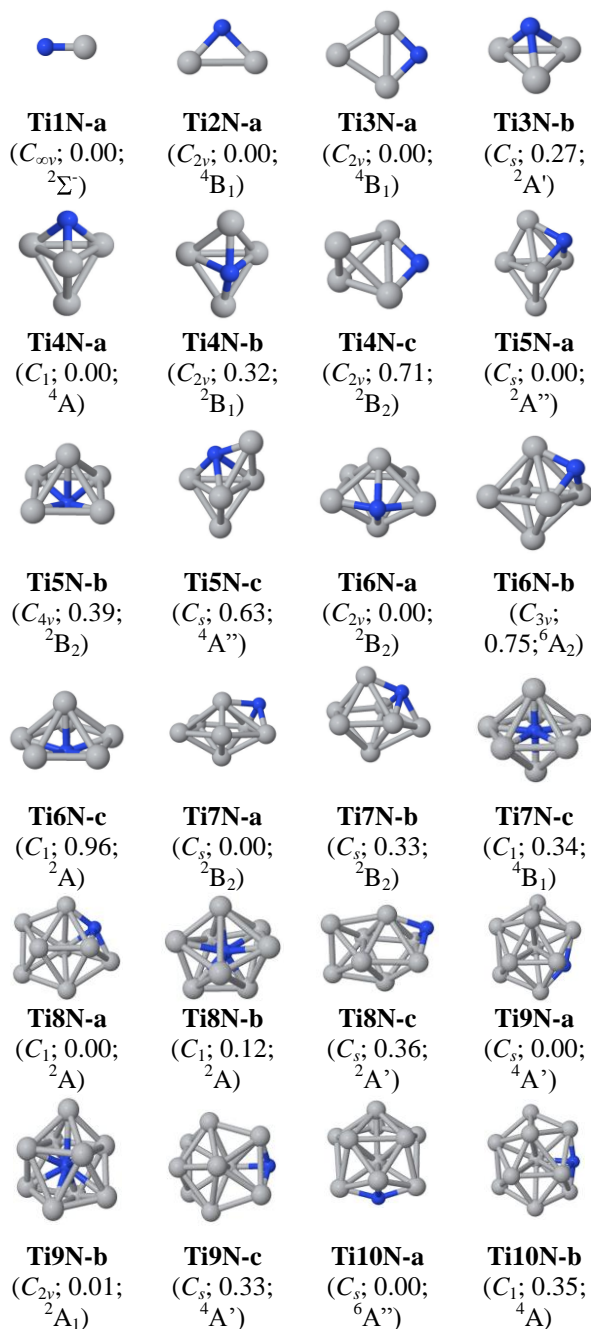

Ti1N-a
($C_{\infty v}$; 0.00; $^2\Sigma^-$)

Ti2N-a
(C_{2v}; 0.00; $^4B_1$)

Ti3N-a
(C_{2v}; 0.00; $^4B_1$)

Ti3N-b
(C_s; 0.27; $^2A'$)

Ti4N-a
(C_1; 0.00; ^4A)

Ti4N-b
(C_{2v}; 0.32; $^2B_1$)

Ti4N-c
(C_{2v}; 0.71; $^2B_2$)

Ti5N-a
(C_s; 0.00; $^2A''$)

Ti5N-b
(C_{4v}; 0.39; $^2B_2$)

Ti5N-c
(C_s; 0.63; $^4A''$)

Ti6N-a
(C_{2v}; 0.00; $^2B_2$)

Ti6N-b
(C_{3v}; 0.75; $^6A_2$)

Ti6N-c
(C_1; 0.96; ^2A)

Ti7N-a
(C_s; 0.00; $^2B_2$)

Ti7N-b
(C_s; 0.33; $^2B_2$)

Ti7N-c
(C_1; 0.34; $^4B_1$)

Ti8N-a
(C_1; 0.00; ^2A)

Ti8N-b
(C_1; 0.12; ^2A)

Ti8N-c
(C_s; 0.36; $^2A'$)

Ti9N-a
(C_s; 0.00; $^4A'$)

Ti9N-b
(C_{2v}; 0.01; $^2A_1$)

Ti9N-c
(C_s; 0.33; $^4A'$)

Ti10N-a
(C_s; 0.00; $^6A''$)

Ti10N-b
(C_1; 0.35; ^4A)

Figure 1: Low-lying isomers of Ti_nN (n = 1-10)

For Ti_6N, the isomers are constructed by substituting a Ti atom of pentagonal bipyramidal Ti_7 unit (D_{5h}) by an N atom (forming **Ti6N-a** and **Ti6N-c** isomers) or adding an N atom into the octahedron Ti_6 (forming **Ti6N-b**). Both **Ti6N-b** and **Ti6N-c** lie quite higher in energy above the ground state (0.75 and 0.96 eV, respectively). At this size, the cage structure appeared, but its relative energy is much higher than the lowest-energy (1.38 eV), so it is not presented in Fig. 1. For n = 7, the **Ti7N-a** and **Ti7N-**

c are established by adding an N atom into pentagonal bipyramid while the **Ti7N-b** has the shape of **Ti8** and replace a Ti atom by an N atom. Especially, for **Ti7N-c**, the N atom added to the center pentagonal bipyramid makes up the cage structure. All these isomers favor the low-spin states (doublet) and the difference in energy is rather small.

For the Ti8N cluster, the lowest-lying isomer (**Ti8N-a**) can be described either as substituted a Ti atom of **Ti9** cluster by an N atom (**Ti8N-a**) or as adding an N atom into bicapped octahedronal structure of **Ti8**. The isomers at low spin state are generally more favourable than higher spin states. Our calculations show that the relative energies of the higher-lying isomers of Ti8N (**Ti8N-b** and **Ti8N-c**) are of 0.12 and 0.36 eV.

For $n = 9$, by substituting an N atom for one top Ti atom of the **Ti10** cluster or adding an N atom into the **Ti9** cluster, we obtain three lowest-energy isomers of the **Ti9N**. Specially, the relative energy of the cage structure **Ti9N-b** is quasi-degenerate with the **Ti9N-a** (differing only 0.01 eV). Thus, both basket-like and cage-like isomers (**Ti9N-a** and **Ti9N-b**) are competitive in the ground state.

For Ti10N, the isomers are also formed similar to the isomers of Ti9N cluster. The lowest-energy isomer (**Ti10N-a**) is formed either by substituting a Ti atom of **Ti11** cluster by an N atom or adding an N atom into **Ti10** cluster (**Ti10N-b**). The lowest-lying isomer is stable at sextet state $^6A"$ while the other at quartet state.

In short, the most stable isomers vary from low-spin state (doublet) to high-spin state (sextet). The three-dimensional structure become favorable from $n=4$. The isomers of Ti_nN clusters are built up either by substituting a nitrogen atom to a facial position of Ti_{n+1} cluster or by adding a nitrogen atom into Ti_n cluster. N atom starts to be encapsulated into the cage to create cage-like structure at the size of $n = 6$. When the cluster size increases, the relative energy of the cage structure decreases from $n = 6$ to $n = 9$. This indicates the stability of these structures increases with this size range. The cage-like structure becomes less stable at the size $n = 10$. It might be that the nitrogen atom is too small to be stable in a large cage.

3.2. Growth mechanism

In this part, the analysis will help to figure out a consistant growth mechanism (either substitution or addition or both) for the Ti_nN ($n = 1$-10) series. To elaborate this growth patterns, the lowest-lying isomers of the ten clusters are summarized in Fig. 2

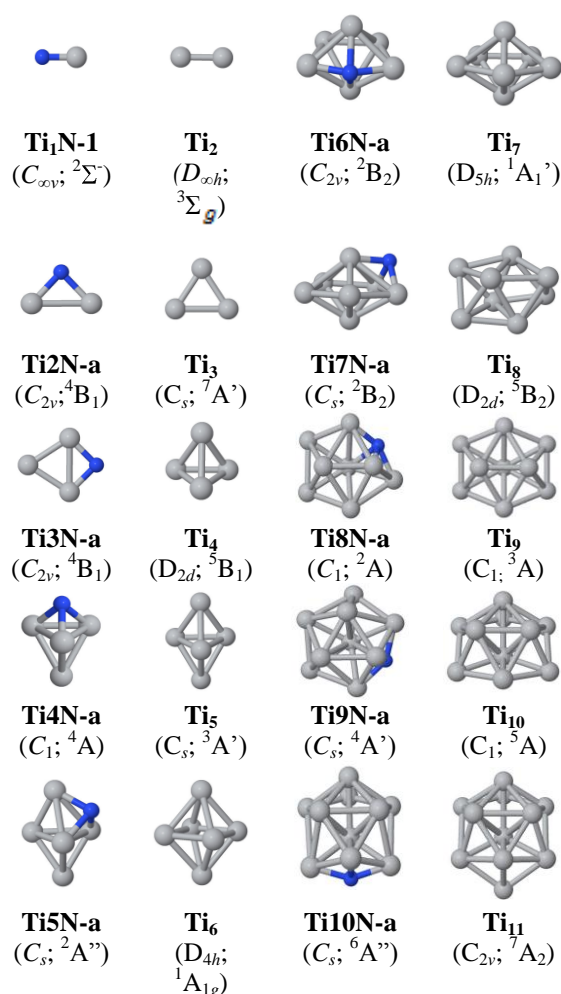together with structures of the pure titanium Ti_{n+1} clusters taken from ref. [5].

Ti1N-1 $(C_{\infty v};\ ^2\Sigma^-)$	**Ti2** $(D_{\infty h};\ ^3\Sigma_g)$	**Ti6N-a** $(C_{2v};\ ^2B_2)$	**Ti7** $(D_{5h};\ ^1A_1')$
Ti2N-a $(C_{2v};\ ^4B_1)$	**Ti3** $(C_s;\ ^7A')$	**Ti7N-a** $(C_s;\ ^2B_2)$	**Ti8** $(D_{2d};\ ^5B_2)$
Ti3N-a $(C_{2v};\ ^4B_1)$	**Ti4** $(D_{2d};\ ^5B_1)$	**Ti8N-a** $(C_1;\ ^2A)$	**Ti9** $(C_1;\ ^3A)$
Ti4N-a $(C_1;\ ^4A)$	**Ti5** $(C_s;\ ^3A')$	**Ti9N-a** $(C_s;\ ^4A')$	**Ti10** $(C_1;\ ^5A)$
Ti5N-a $(C_s;\ ^2A")$	**Ti6** $(D_{4h};\ ^1A_{1g})$	**Ti10N-a** $(C_s;\ ^6A")$	**Ti11** $(C_{2v};\ ^7A_2)$

Figure 2: Growth mechanisms of Ti_{n+1} and Ti_nN clusters

In this series, seven clusters out of ten clusters are formed by substituting an N atom to position of Ti_{n+1} cluster, including TiN, Ti2N, Ti4N, Ti6N, Ti8N, Ti9N and Ti10N. Thus, three clusters, namely Ti3N, Ti5N and Ti7N, do not follow the substitution rule. Considering the addition rule for this series, all of the ten Ti_nN clusters are formed by adding nitrogen atom to surface of the Ti_n clusters. In particular, Ti2N, an isosceles triangle (C_{2v}), formed by adding an N atom on Ti2. Ti3N, a planar quadrangle, is created by adding an N atom on an edge of the triangle Ti3. Ti4N, a distorted triangular bipyramid with the N atom at an apex, is formed by adding the N atom on a triangular face of the tetrahedron Ti4. Ti5N, an N-face-capped triangular bipyramid, is formed by adding an N atom on a triangular face of the trigonal bipyramid Ti5. Ti6N, a pentagonal bipyramid, is formed by adding an N atom on an

edge of the octahedron Ti_6 resulting the Ti-Ti bond cleavage then creating the pentagon with an vertex occupied by the N atom. Ti_7N, an N-face-capped pentagonal bipyramid, is formed by adding an N atom on a triangular face of the pentagonal bipyramid Ti_7. Ti_8N, adopting a structure similar to Ti_9, can be formed by adding an N atom on a face of the dodecahedron bisdisphenoid Ti_8 resulting the cleavage of a Ti-Ti bond. The Ti_9N and $Ti_{10}N$ clusters are also formed in a similar way to Ti_8N. Thus, the whole series Ti_nN (n = 1-10) are formed by addition a nitrogen atom to an edge or a face of the corresponding pure Ti_n cluster, which resembles the formation of Ti_nO clusters [16].

In conclusion, the growth mechanism of Ti_nN clusters can be better described by nitrogen-addition rule.

Considering the cage structure wherein the N atom is encapsulated inside a titanium cage, it starts to form when n = 6 and has lowest relative energy (0.01 eV) at n = 9. When the size increases, this structure becomes unfavorable. This trend is different from the clusters of metalloid elements such as silicon or germanium which start to form cage structures with transition metal dopants at a certain size onwards. Even, the P-doped titanium cluster was found to form cage structure from n = 10 onwards [6]. This indicates a something different in chemical bonding of the N atom with the Ti atoms. Indeed, phosphorus belongs to period three with vacant 3d-orbitals available to make bonds, while nitrogen has only four obitals (2s and 2p) available for bonding. Therefore, when the cage composed of too many Ti atoms, the N atom cannot make bonds with all.

3.3. Stability of clusters

In this section, we investigate the trends of stability of the N-doped clusters as compared with the pure titanium clusters.

3.2.1. *Average binding energies*

For Ti_nN and Ti_{n+1} clusters the expression for the averaged binding energy (E_b) has the following form:

$$E_b(Ti_nN)=[E(N)+nE(Ti)-E(Ti_nN)]/(n+1) \quad (1)$$

$$E_b(Ti_{n+1})=[(n+1)E(Ti)-E(Ti_{n+1})]/(n+1) \quad (2)$$

Where E(X) is total energy corrected by zero-point energy of the ground-state energy of the system X. The variation of averaged binding energy of the Ti_nN cluster to the cluster size is shown in Fig. 3a.

It can be seen that the average binding energies of Ti_nN clusters increase monotonically with cluster size. The doping of an N atom enhances the binding energy of the host clusters, which implies that the doping of the N atom may improve the stability. This might be due to the stronger Ti–N bond than Ti–Ti bond whose binding energies are 2.89 and 1.37 eV, respectively, which are calculated using the same level of theory in this present work.

The difference between the binding energies per atom for Ti_{n+1} and Ti_nN lies in the range from 1.52 eV for n = 1 to 0.39 eV for n = 10. The enhancement in binding energy is small for large clusters. This phenomenon is also presented in B-doped Ti clusters [17]. We could explain this phenomenon as follows: as the clusters evolve, the Ti-N coordination numbers increase, whereas the increasing Ti-N coordination number weakens the interactions between Ti and N atoms. Interestingly, there is a special enhancement in binding energy of Ti_7 and Ti_6N clusters. These features indicate a special stability of Ti_7 and Ti_6N clusters in the series of Ti_{n+1} and Ti_nN clusters.

3.2.2. *Second-order energy differences*

For further investigation of the stability of pure and N-doped titanium clusters, the second-order difference of the total energies, $\Delta^2E(n)$, was calculated. The function Δ^2E is defined as:

$$\Delta^2E = E(n+1) + E(n-1) - 2E(n) \quad (3)$$

The second-order differences of total energies ($\Delta^2E(n)$) for the lowest energy structures of both systems with sizes of n = 1-10 are also evaluated and plotted as a function of cluster size in Fig. 3b.

As seen in Figure 3b, the Ti_5 and Ti_7 clusters with positive Δ^2E values have stronger stabilities relative to their respective neighbors. The Ti_nN clusters show three peaks at Ti_4N, Ti_6N and Ti_8N, respectively, indicating the higher stabilities of these clusters comparing to their neighbors. A prominent maximum for the Ti_7 cluster is also detected with the doping of an N atom in Ti_6N cluster. The pentagonal bipyramid structure with D_{5h} symmetry is an extremely stable structure. Besides, the substituting one Ti atom by N in Ti_7 cluster does not significantly change the geometry, in the other words, the Ti_6N cluster hold similar geometry to the host Ti_7 cluster. Thus, one suspects that the similar shape of Ti_6N and Ti_7 clusters may be one of the main reasons for the stability of Ti_6N.
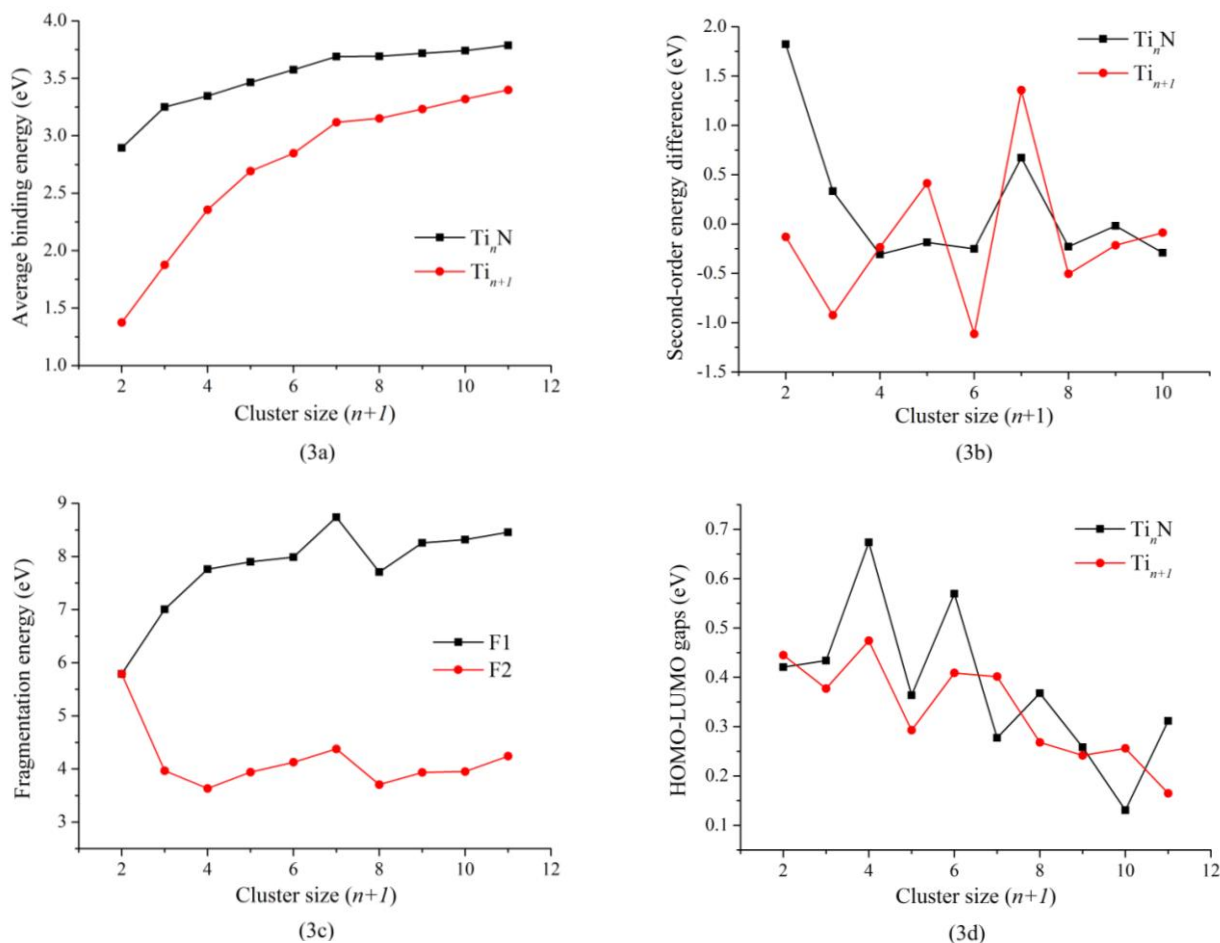
Figure 3: Graphs showing size-dependence of average binding energies (3a), second-order energy differences (3b), fragmentation energies (3c) and HOMO-LUMO gaps (3d) of Ti_{n+1} and Ti_nN clusters

3.2.3. Fragmentation energies

To confirm the relative stabilities of the Ti_nN clusters, fragmentation energies F (eV) are computed and then plotted in Fig. 3c. Here, we consider two fragmentation channels which either removes a Ti atom or an N atom from the Ti_nN cluster. The fragmentation energies are defined as:

$$F1(Ti_nN) = E(N) + E(Ti_n) - E(Ti_nN) \qquad (4)$$

$$F2(Ti_nN) = E(Ti_{n-1}N) + E(Ti) - E(Ti_nN) \quad (5)$$

Fig. 3c shows that the N-dissociations cost much more energy than the Ti-dissociation, meaning that the N atom bonds with cluster stronger than the Ti atom. In both channels, the Ti_6N cluster appears to have higher dissociation energies than others, suggesting its higher stability once more.

3.2.4. HOMO-LUMO gaps

As we know, the gaps between the highest occupied MO and lowest unoccupied MO (HOMO-LUMO gaps) are a useful quantity to assume the electronic stability of a system. Figure 3d shows us the HOMO-LUMO gaps for the most stable isomers of the studied Ti_{n+1} and Ti_nN clusters. Both Ti_{n+1} and Ti_nN clusters have quite low HOMO-LUMO gaps, ranging from 0.1-0.7 eV. This refers that doping with an N atom has not made a significant change in the band gaps of the titanium clusters.

4. CONCLUSIONS

Some concluding remarks are resulted from this theoretical study as follows:

- The most stable isomers may have spin state ranging from doublet to quartet to sextet.
- The ground-state structure of these clusters are built up by the nitrogen-addition rule. Thus, the nitrogen atom prefers to stay on surface of the clusters.
- Doping with one N atom increases the stability of titanium clusters and decreases their metallicity.
- The analyses of average binding energy, second-order energy differences and fragmentation energy according to cluster size show that Ti_6N cluster is endowed with special stability.

REFERENCES

1. J. A. Alonso. *Electronic and atomic structure, and magnetism of transition-metal clusters*, Chem. Rev., **100**, 637 (2000).
2. R. Ferrando, J. Jelline, R. L. Johnson. *Nanoalloys: from theory to applications of alloy clusters and nanoparticles*, Chem. Rev., **108**, 845-910 (2008).
3. J. Xiang, S. H. Wei, X. H. Yan, J. Q. You, Y. L. Mao. *A density-functional study of Al- doped Ti clusters: Ti$_n$Al (n = 1-13)*, J. Chem. Phys., **120**, 4251 (2004).
4. S. Y. Wang, W. Duan, C. Y. Wang. *First-principles investigation into the structural stability of icosahedral Ti$_{12}$X clusters (X = B, C, N, Al, Si, P, V, Cr, Mn, Fe, Co and Ni)*, J. Phys. B: At. Mol. Opt. Phys., **35**, 4015 (2002).
5. V. V. Alexey, H. Matthias, V. Y. Alexander, V. S. Andrey. *Characterization of small pure and Ni-doped titanium clusters: ab initio versus classical approaches*, Computational Materials Science, **76**, 80-88 (2013).
6. H. Wang, N. Hu, D. -J. Tao, Z. -H Lu, J. Nie, X. -S. Chen. *Structural and electronic properties of phosphorus-doped titanium clusters: A DFT study,* Computational and Theoretical Chemistry, **977**, 50-54 (2011).
7. M. J. Frisch and et al. Gaussian 03 (Revision E.01), Gaussian, Inc., Wall (2008).
8. J. P. Perdew and J. Wang. *Accurate and simple analytic representation of the electron-gas correlation energy,* Phys. Rev. B, **45**, 13244 (1992).
9. J. J. Zhao, Q. Qiu, B. L. Wang, J. L. Wang, and G. H. Wang. *Geometric and electronic properties of titanium clusters studied by plane-wave ultrosoft pseudopotential*, Solid State Commun., **118**, 157 (2001).
10. M. Castro, S. R. Liu, H. J. Zhai and L. S. Wang. *Structural and electronic properties of small titanium clusters: an anion photoelectron spectroscopy and density functional study*, J. Chem. Phys., **118**, 2116 (2003).
11. T. J. D. Kumar, P. F. Weck, and M. Balakrishnan. *Evolution of small Ti clusters and the dissociative chemisorption of H$_2$ on Ti*, J. Phys. Chem. C, **111**, 7494 (2007).
12. C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dodds, and D. A. Dixon. *A local density functional study of the structure and vibrational frequencies of molecular transition-metal compounds*, J. Phys. Chem., **96**, 6630 (1992).
13. A. Anderson. *Structures, binding energies, and charge distributions for two to six atom Ti, Cr, Fe, and Ni clusters and their relationship to nucleation and cluster catalysis*, J. Chem. Phys., **64**, 4046 (1976).
14. M. S. Villanueva and et al. *Stable Ti$_n$ (n = 2-15) clusters and their geometries: DFT Calculations*, J. Phys. Chem. A, **110**, 10274 (2006).
15. S. H. Wei, Z. Zeng, J. Q. You, X. H. Yan, X. G. Gong. *A density-functional study of small titanium clusters*, J. Chem. Phys., **113**, 11127 (2000).
16. Z. H. Lu, J. X. Cao. *First-principles calculations for titanium monoxide clusters Ti$_n$O (n = 1-9)*, Chin. Phys. B, **17**, 3336 (2008).
17. J. G. Du, X. Y. Sun, J. Chen, G. Jiang. *The changes in the geometrical, electronic and magnetic properties of titanium clusters as one titanium atom is substituted by boron*, J. Phys. B: At. Mol. Opt. Phys., **43**, 205103 (2010).

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