ISSN: 2586-7652 (Print) Vol. 04, No. 02, September 2021
ISSN: 2635-7607 (Online)
International Journal of Advanced Engineering
Source: http://ictaes.org
Manuscript received: April 10, 2021; Revised: May 15, 2021; Accepted: June 2, 2021

Computational Study of Adsorption of Di-nitrogen on Small Bimetallic Clusters Hf_mTa_n

R. Acharya[1],†, N. Pant[1],†, R. Simkhada[2], S. Shrestha[3],V. K. Jha,[1]*

[1]*Department of Physics, St. Xavier's College, Maitighar, Kathmandu, Nepal*

[2]*Department of Physics, Amrit Science Campus, Lainchour, Kathmandu, Nepal*

[3]*Department of Electronics & Computer Engineering, Pulchowk Campus, Institute of Engineering, Tribhuvan University, Lalitpur, Nepal*

† both authors have equal contribution,

Abstract

Density functional theory (DFT) calculations are performed to investigate N2 adsorption on small bimetallic HfmTan clusters (where m+n ≤ 4). The dissociation of N-N bond is found to be strongly dependent on orientation of N-N axis with respect to the axis of the adsorbent cluster. Orientation of N-N axis, whether perpendicular or parallel, to cluster axis has been found to be suitable for dissociative adsorption of di-nitrogen depending upon geometries and size of clusters. It is found that the adsorption energies of HfmTan clusters differs significantly on varying sizes and configurations. Our study also shows that even dimer can dissociate di-nitrogen completely..

Keywords: *Density Functional Theory (DFT), Adsorption, Bimetallic, Configurations, Transition Metals (TM)*

1. Introduction

In The study of small metal clusters have gained considerable attentions, both experimentally and theoretically, as new functional nano-materials or solid-state materials due to their scientific interests and technological applications. Clusters show different chemical and physical properties and functionalities from their

Corresponding Author : V. K. Jha
Author's affiliation:Dept. of Physics, St. Xavier's College, Maitighar, Kathmandu, Nepal
Email: vkjha@sxc.edu.np
Copyright © ICT-AES

bulk metal form. These properties and functions undergo relevant changes depending on number of constituent atoms, shapes and sizes. Nowadays, adsorption behavior of many gas molecules on clusters of noble and transition metals are being studied, and it has been found that adsorption properties changes strongly with the increasing number of clusters size for many synthesis such as H2 on Pt [1], O2 on Au [2], N2 on Ta [3] and so on. In the last few decades, the adsorption and desorption of N2 molecules on the several metals have been studied [2,3,5,6]. The researchers have been trying continuously to break the strong triple bond of di-nitrogen for several years. The challenges of early 20th century are still remained today to convert atmospheric nitrogen to ammonia. This was responded and widely used till today by Haber-Bosch Process [4]. But this requires high temperature and high pressure. Therefore, several alternatives for synthesis of ammonia had been studied to minimize the energy cost for breaking the strong triple bond of di-nitrogen. In recent years, several attempts have been explored to weaken and dissociate this strongest bond. Some attempts were successful with transition metallic clusters. In 2009, Roy et al. [5] with hybrid-GGA B3LYP functional approach has studied the adsorption of nitrogen molecule on model lithium clusters employing density functional theory. They found that at-least 8-atoms of lithium clusters is essential for the complete cleavage of triple bond of di-nitrogen. In 2010, Yadav et al. [3] studied that the global minimum structures of dimer, trimer and tetramer clusters of tantalum adsorb nitrogen molecule in a dissociative manner. The most of the studies on adsorption have been carried out on homogeneous clusters. In 2011, Song et.al. [2] studied CO and O2 adsorption as well as CO oxidation on the AumPdn (m + n = 2 to 6) bimetallic clusters. It was found that the adsorption energies of both CO and O2 on bimetallic clusters are greater than those on the pure gold clusters of corresponding sizes. In 2020, R. Acharya et al. [6] shows the nature of adsorption is dissociative or not, depends on the orientation of adsorbate N2 molecule. Also, bimetallic clusters enhance N-N bond length compared to the mono-metallic case. Motivated by these study here we have attempted to explore the prospects of di-nitrogen dissociation on bimetallic clusters. In this present work, we have selected various possible orientation of adsorbate di-nitrogen for dimers, trimers and tetramers of HfTa clusters in comparison with those on the corresponding pure Hf and Ta clusters. Thus, the study of bimetallic clusters can help in clarifying the properties of impurities. No studies have been reported on the adsorption of molecular nitrogen on bimetallic HfTa clusters (except dimers) till now.

2. Computational Details

In this study, all the calculations are based on plane-wave density functional theory (DFT) and are performed using the quantum espresso (QE) [7,8] package. The electron-ion interactions are represented by the projector-augmented wave (PAW) [9,10] approach and the exchange correlation energies are described by a generalized-gradient approximation (GGA) using the Perdew Burke Ernzerhof (PBE) [11,12] functional with a plane-wave expansion with a cutoff of 46 Ry. The size of the super-cell was taken to be large enough (cube of sides 15 A˚) to avoid specious interaction between images with the energy convergence threshold of 107 Ry. We know the reactions between clusters and N2 molecule may arise a large variety of geometrical structures. So, in order to obtain the global lowest energy structures of HfmTan clusters, first clusters were considered as initial candidates and are optimized for the most stable states. These stable optimized structures are chosen as ground-state geometry where N2 molecule with different orientations are adsorbed. The selected configurations for N2 adsorption are shown in figure 1. In the configurations '1a', '2a', '3a', '4a' and '5a', N-N axis is parallel to HfmTan clusters and in the configurations '1b', '2b', '3b', '4b' and '5b', N-N is vertically perpendicular to HfmTan clusters at top-site. Similarly, in the configurations '2c', '3c', '4c' and '5c', N-N is vertically perpendicularly placed at equatorial site of HfmTan clusters. The configurations '2e' and '4f' have N-N perpendicularly placed to HfmTan clusters at bridge-site. In the configurations '2d', N-N axis is horizontally perpendicular to HfmTan clusters at

top-site and in the configurations '3e', '4d' and '5e', N-N axis is placed parallel to the base two-atoms at equatorial site. In the configurations '4e' and '5d', N-N axis is perpendicularly placed between two base atoms and '3d' is placed horizontally perpendicular with two base atoms at equatorial-site as shown in Figure 1. The figures used in this paper are visualized using Xcrysden software [13].

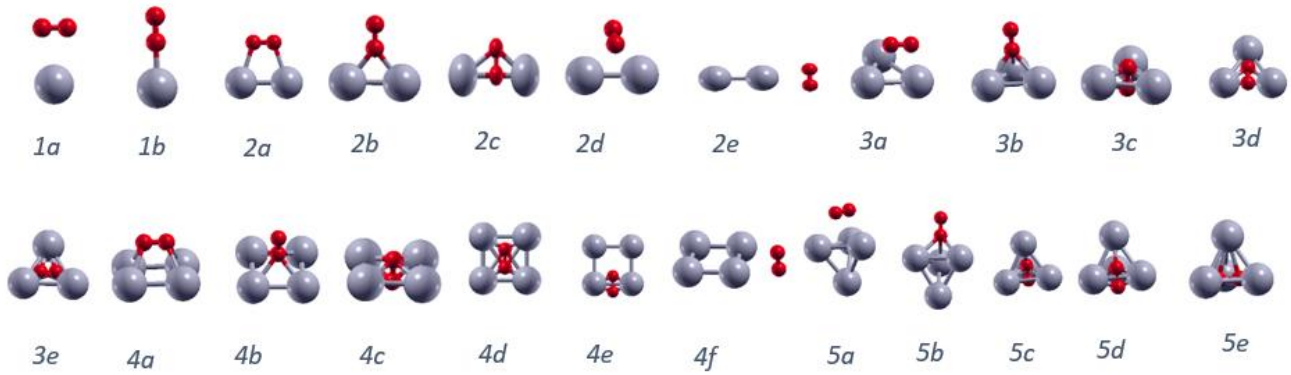


Figure 1. The most stable structures of HfmTan clusters with the N2 adsorption configurations. Large spheres represent TM atoms and small spheres represent N-atoms.

3. Results and Discussions

The main aim of our current work is to study and find alternative way to minimize the energy cost for breaking the strong triple bond of di-nitrogen. In this calculation, first we studied the adsorption and dissociation of di-nitrogen on mono-metallic clusters. The results of these pure clusters will be helpful in comparing and analyzing the results of adsorption on bimetallic clusters. The study is based on similar initial configurations of atomic positions. The results from computational setup for dinitrogen and optimized clusters are compared with the experimental results for their validity and accuracy. The computed bond length and binding energy of di-nitrogen are 1.1Ao and 7.69 eV resp [14]. Here, the adsorption energies (Ead) of N2 molecule adsorbed on metallic clusters HfmTanN2 (where m+n $\leq$ 4)) is calculated by using the equation (1).

$$E_{ad}(N_2) = E(Hf_mTa_n) + EN_2) - E(Hf_mTa_nN_2) \quad (1)$$

where E(HfmTan), E(N2) and E(HfmTanN2) are the calculated lowest energies of the HfmTan clusters, N2 molecule and HfmTanN2 clusters respectively

2.1 Adsorption of dinitrogen on bimetallic clusters HfmTan clusters (m+n = 1)

In Figure 2, N2 adsorbed structures on various configurations are shown. N2 doesn't dissociate when it is adsorbed on hafnium atom. The calculated bond-length and adsorption energy are 1.25 Ao and 1.24 eV respectively for '1a' configuration. The bond length is slightly elongated with N-Hf-N angle of 35.9o. In '1b' configuration there is also a partial dissociation of N-N bond length of 1.16 Ao with adsorption energy of 1.23 eV. Similarly, for Ta-atom, there is almost degenerate in 1a configuration with fully dissociated N-atoms with N-Ta-N angle of 56.6 o. This calculated result of Ta-atom well agrees with previous calculated binding energy of 1.70 eV for elongation of 2.68 Ao [3]. However, in second linear '1b' configuration there is partial dissociation. This shows Ta-atom is more energetically favorable than Hf-atom for similar case. Although Hf-atom of configuration '1a' shows more efficiency, consuming less adsorption energy compared to that of Ta-atom for stretching N-N bond length.

.



Figure 2. Optimized global minimum structures of HfmTan clusters (m+n = 1) in different configurations with adsorbed N2. The first entry in the labels represents the adsorption energy of the cluster (in eV) and the second entry represents the elongation of N2 (in Ao). The gray, yellow and red balls represent Hf, Ta and N atoms, respectively.

2.2 Adsorption of dinitrogen on bimetallic clusters HfmTan clusters (m+n = 2)

Figure 3 shows N2 adsorbed bimetallic dimers on various configurations '2a' to '2e'. For Hf-dimers (optimized structure shown in first row) the calculated bond length of Hf2 dimer (2.46 Ao) is in good agreement with previous calculated result of 2.46 Ao by using Guggenheimer's rule [15] and 2.63 Ao by using DFT [16]. Similar to Hf-atom, here N2 doesn't dissociate when it is adsorbed to Hf-dimers. However, in all configurations there is cleavage of N-N triple bond as N-N distances in '2c' and '2d' configurations are greater than N-N single bond length of 1.49 Ao [6]. In '2a' configuration is greater than N-N double bond length of 1.25 Ao [6] and in other remaining configurations are also greater than N-N triple bond length of 1.10 Ao .The configuration '2a' leads to Hf-N-N-Hf linear-chain, this could be due to the strong Hf-N interaction [6]. For the elongation of same bond length N-N the configuration '2b' consumes 0.81 eV less adsorption energy than the configuration '2e' and configuration '2c' require 0.21 eV less adsorption energy than configuration '2d'. This shows configuration '2c' is more favorable on the perspective of energy consumption for elongation of N2 bond length. Thus, configurations N-N axis perpendicular to Hf-Hf dimers is suitable, which well agrees with previous reported value [6]. For Ta-dimers (optimized structure shown in third row), our calculated distance of 2.16 Ao which satisfies previous theoretical results (2.15 Ao) [16]. Similar to Ta-atom here, N2 dissociates when it is adsorbed to Ta2 dimers (configurations 2c and 2d). However, there is partial dissociation in remaining configurations, there is cleavage of N-N triple bond as N-N distance in '2a' configuration is greater than N-N double bond length and in the configurations '2b' and '2e' are greater than N-N triple bond length. Here, configuration '2e' is favorable than 2), since 2e has less adsorption energy for stretching N2 comparatively. Similarly, same reason holds for '2d' being favorable behind '2c'. As a whole, the configuration '2d' is more favorable although '2c' holds more adsorption energy. For HfTa dimer (optimized structure shown in second row), the calculated distance of bond length of HfTa is 2.25 Ao. Here, N2 dissociates when it is adsorbed to HfTa dimer (configurations 2c and 2d). However, there is partial dissociation in remaining configurations, there is cleavage of N-N triple bond as N-N distances in '2a' and '2b' configurations are greater than N-N double bond length and in the configurations 2e and 2e* are greater than N-N triple bond length. The calculated values are shown in figure 3. Unlike to homogenous clusters, the top-site configurations either vertical-perpendicular (configuration 2b) or parallel (configuration 2a) to adsorbent dimer, the result is insignificant. Both have 1.32 Ao elongation of N-N bond length with similar adsorption energy of 2.80 eV. However, top-site and equatorial site orientation of dinitrogen is affected which is observed in the configurations '2c' and '2d'. This shows the configuration 2d is efficient for adsorption whereas '2c' is more favorable energetically. Similarly, '2e' and '2e*' are on same configurations as shown in figure 1 differing on adsorbing position site on N2. Here, '2e' configuration with edge-site of Ta-atom with N2 and '2e*' with Hf atom. The calculated values show the configuration '2e*' is efficient by 0.271 eV than the configuration

'2e'. This reveals Hf-site adsorption is more efficient for minimizing the adsorption energy. Therefore, horizontal-perpendicular at top-site, configuration '2d' is most suitable for efficiency and perpendicular at equatorial-site. The configuration '2c' is energetically most favorable, which well agrees with previous theoretical values [6]. It is observed from properties of different configurations, the HfTa-dimers ensembles to properties of Ta-dimers. However, bimetallic cluster is more energetically favorable than pure Hf-clusters and Ta-clusters.

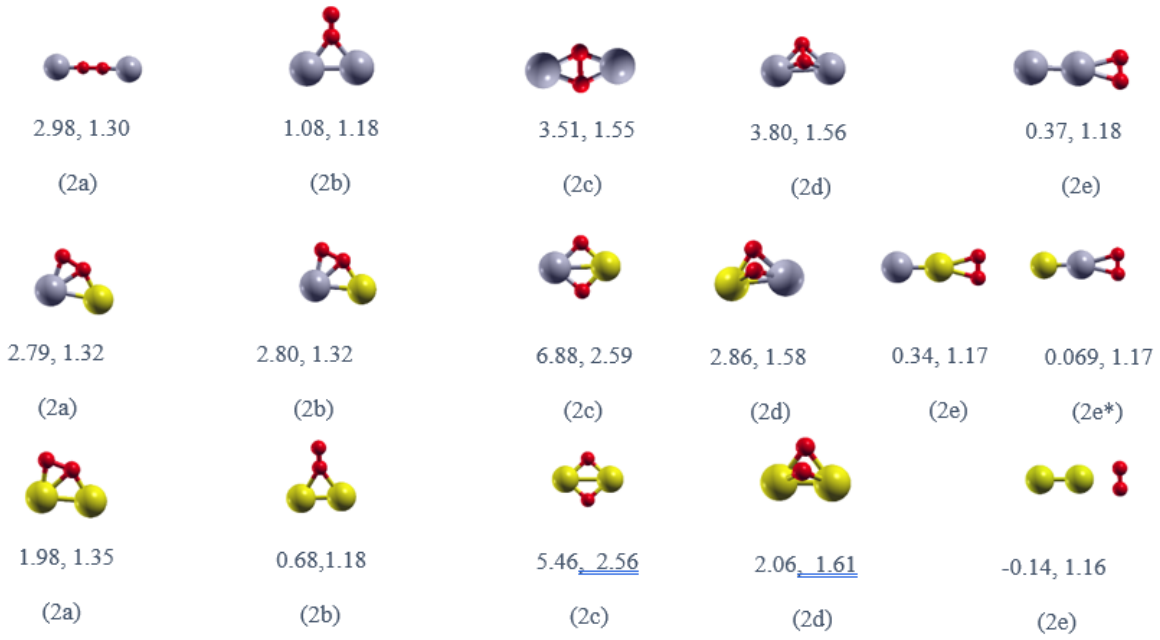


Figure 3. Optimized global minimum structures of HfmTan clusters (m+n = 2) in different configurations with adsorbed N2. The first entry in the labels represents the adsorption energy of the cluster (in eV) and the second entry represents the elongation of N2 (in Ao). The gray, yellow and red balls represent Hf, Ta and N atoms, respectively. Here * denote adsorption of N2 on other atomic site.

2.3 Adsorption of dinitrogen on bimetallic clusters HfmTan clusters (m+n = 3)

Figure 4 shows N2 adsorbed bimetallic trimers on various configurations '3a' to '3e'. For Hf trimers, the optimized structure for Hf3 features equilateral triangle with bond length 2.67 Ao. The selected configurations (3a to 3e) of N2 orientations with adsorbent Hf3 and N2 adsorbed are shown in figure 4. The complete cleavage of bond-length of N-N occurs in the configurations '3a', '3c' and '3d', whereas cleavage of second and triple bond-length of N2 is observed in configurations '3e' and '3b' resp. Here '3c' configuration is energetically favorable and '3d' configuration is most favorable as less energy is required to dissociate dinitrogen. Interestingly, the configurations '3d' and '3e' is also able to break Hf3 triangular structure. For Ta-trimers , the optimized structure for Ta3 features the equilateral triangle with bond length 2.43 Ao.

The selected configurations (3a to 3e) of N2 orientations with adsorbent Ta3 and N2 adsorbed are shown in figure 4. The complete cleavage of bond-length of N-N occurs in '3c', '3d' and '3e' configurations, whereas cleavage of second and triple bond length of N2 is observed in '3a' and '3b' resp.

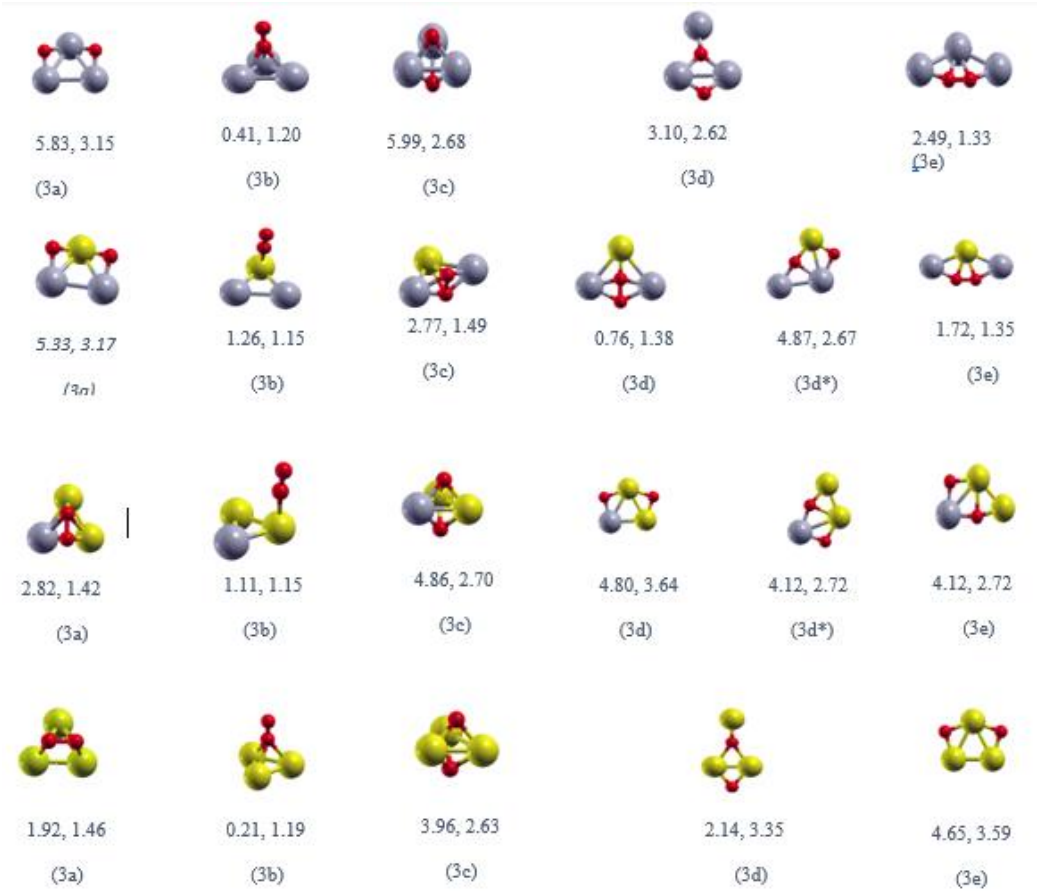


Figure 4. Optimized global minimum structures of HfmTan clusters (m+n = 3) in different configurations with adsorbed N2. The first entry in the labels represents the adsorption energy of the cluster (in eV) and the second entry represents the elongation of N2 (in Ao). The gray, yellow and red balls represent Hf, Ta and N atoms, respectively. Here * denote adsorption of N2 on other atomic site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

Here, configuration '3d' is favorable, however, '3c' configuration is more energetically favorable. The adsorption energy required to dissociate bond length of N-N is less. Here all the configurations has less adsorption energy as compared to those of Hf-trimers. The configuration '3d' structure is able to break Ta3 triangular structure. For bimetallic HfTa trimer, ground-state structure characterizes the isosceles triangle with Hf-Hf/Ta-Ta and HfTa bond length of 2.72 Ao and 2.52 Ao for Hf2Ta and 2.36 Ao and 2.58 Ao for HfTa2 respectively. The selected configurations (3a to 3e) of N2 orientations with adsorbent HfmTan (m+n=3) and N2 adsorbed are shown in figure 4. In Hf2Ta, the complete cleavage of bond-length of N-N occurs in '3a' ,'3a*' and '3d*' configurations, whereas cleavage of single bond length of N2 is seen in configuration '3c', second bond length of N2 is observed in '3d' and '3e', and cleavage of triple bond-length of N2 is observed in '3b'. Among studied configurations, '3a' configuration is energetically favorable and '3d' configuration is most favorable, in the sense that less energy is required to dissociate dinitrogen. In the configuration '3d', N2 is placed to Hf-Hf site whereas in the configuration '3d*' is placed on Hf-Ta site. The calculated values show N2 dissociates completely in HfTa site consuming more adsorption energy. This shows the orientation of dinitrogen favors bimetallic site. In HfTa2, the complete cleavage of bond-length of N-N occurs in '3c', '3d', '3d*' and '3e'

configurations, whereas cleavage of second bond length of N2 is observed in '3a' and '3a*' and cleavage of triple bond-length of N-N is observed in '3b'. Here, '3c' configuration is energetically favorable, and '3d' and '3d*' configurations are most favorable, as less energy is required to dissociate dinitrogen. In the configuration '3d', N2 is placed to Ta-Ta site whereas in the configuration '3d*' is placed on Hf-Ta site. The calculated values show N2 dissociates completely in the both sites. The configuration '3d' has adsorption energy of 4.80 eV for stretching 3.64 Ao of bond length of dinitrogen, this shows Ta-Ta site is efficient. The adsorption energy of pure Hf-trimers is more than pure-trimers for same elongation of dinitrogen. The presence of impurities with varying orientations of N2 differ in results. The adsorption energy is seen more in bimetallic configurations. HfTa2 resembles similar properties to Ta3 in various configurations consuming more adsorption energy..

2.4 Adsorption of dinitrogen on bimetallic clusters HfmTan clusters (m+n = 4)

2.4.1 Square-shaped

For tetramers, the ground-state structures here features the square-shaped (configurations 4a to 4f). These selected configurations of N2 orientations with adsorbent tetramer is shown in Figure 5. For squared-shape Hf-tetramers, the N2 adsorbed structures results distorted rhombus structures (Figure 5 first row). The optimized Hf4 tetramer obtained here have Hf-Hf bond length of 2.62 A˚. The complete cleavage of bond length of N-N occurs in '4a', '4b', '4d', '4e' and '4f' configurations, whereas cleavage of single bond-length of N2 is observed '4c' configuration. '4a' configuration is energetically favorable and '4d' configuration is most favorable as less energy is required to dissociate dinitrogen. '4d' configuration is able to break ground state rectangular shape. The optimized Ta4 tetramer has Ta-Ta bond length 2.43 A˚. The N2 adsorbed structures results distorted rhombus structures (figure 5 last row). The complete cleavage of bond-length of N-N occurs in '4c', '4d' and '4e' configurations, whereas cleavage of double bond length of N2 is observed '4a' and '4f' configurations and cleavage of single-bond length of N2 is observed in '4b'. '4d' configuration are energetically more favorable whereas '4e' configuration is most favorable as it has comparatively less adsorption energy than other configurations. Similar to Hf4 , '4d' configuration is able to break Ta4 tetramer structure. For bimetallic tetramers HfmTan (m+n = 4), the tetramer structure can also be formed with several constituents, Hf3Ta (3Hf and 1Ta atoms), Hf2Ta2 (2Hf and 2Ta atoms) and HfTa3 (1 Hf and 3Ta atoms). Hf2Ta2 further can be arranged with two Hf-Hf atoms alternately and in pairs. These N2 adsorbed optimized structures with different constituents are shown row-wise in figure 5. For Hf3Ta (Figure 5 second row), the bond length of Hf-Ta, Hf-Hf are 2.69 A˚ and 2.49 A˚. The complete cleavage of bond-length of N-N occurs in '4c', '4d' and '4f*' configurations, whereas cleavage of double bond length of N2 are observed in '4a', '4e*' and '4e', and cleavage of triple bond-length of N-N are observed in '4b' and '4f'. The configuration '4d' has adsorption energy of 1.71 eV for breaking bond length of dinitrogen completely. So, this configuration is suitable, however, the configuration '4c' is energetically favorable. For Hf2Ta2 (Figure 5 third row), Hf-Ta bond length is 2.53 A˚. The complete cleavage of bond-length of N-N occurs in '4a', '4c', '4d' and '4f' configurations, whereas cleavage of double bond length of N2 is observed in '4e' and cleavage of triple bond-length of N-N is observed in '4b'. The configuration '4c' has adsorption energy of 3.11 eV for

breaking bond length of dinitrogen completely. So, this configuration '4c' is suitable, however, the configuration '4a' is energetically favorable. For Hf2Ta2 (figure 5 fourth row), Hf-Hf, Hf-Ta and Ta-Ta bond length are 2.76 A˚, 2.52 A˚ and 2.31 A˚. The complete cleavage of bond-length of N-N occurs in '4a', '4c', '4c*', '4d', '4e', '4e*' and '4f' configurations, whereas cleavage of double bond length of N2 is observed in '4b' and '4f*'. The configuration '4c*' has adsorption energy of 4.07 eV for breaking bond length of dinitrogen with 4.55 A˚ completely. Configuration '4c*' is suitable, however, the configuration '4a' is energetically favorable.

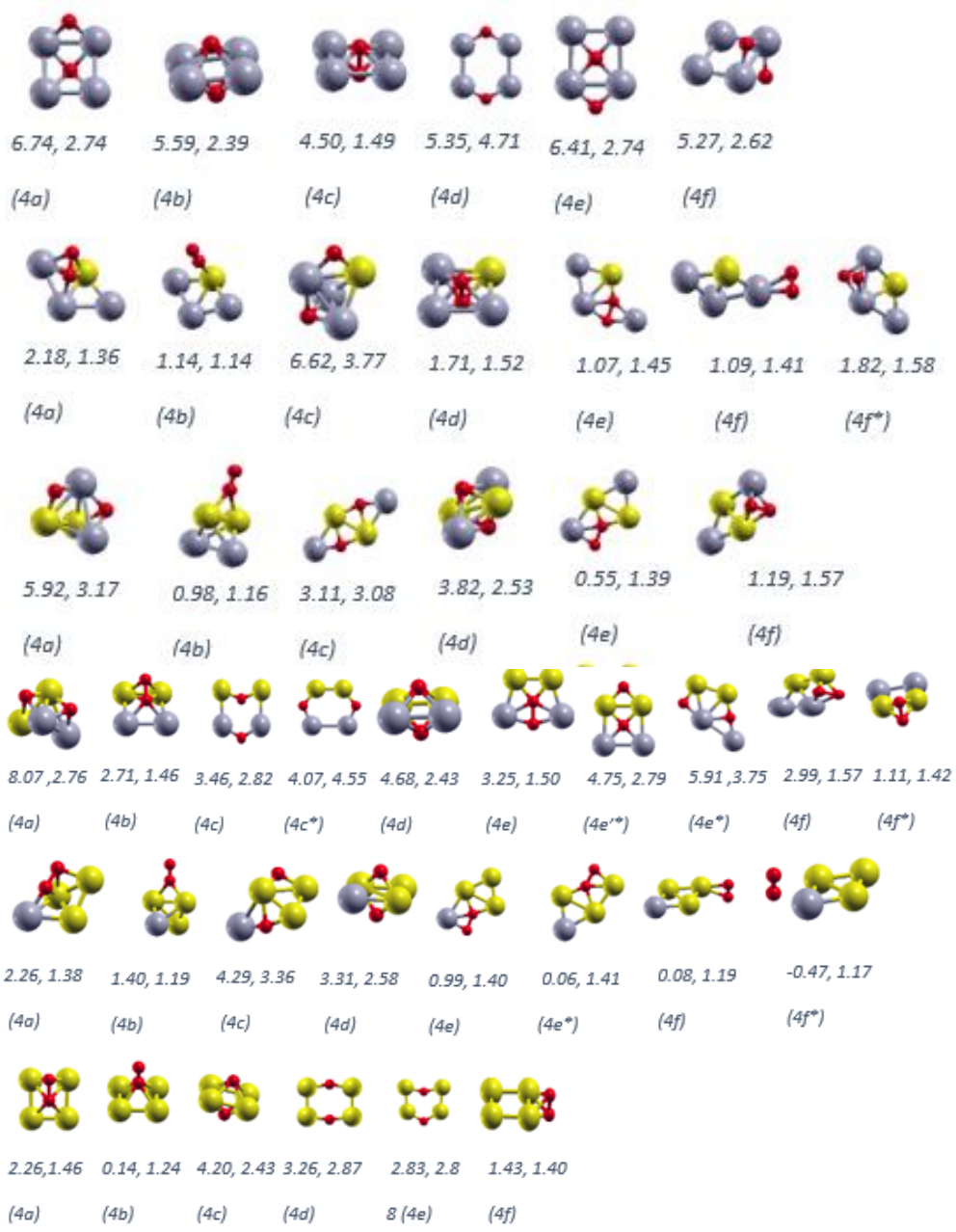


Figure 5. Optimized global minimum structures of HfmTan clusters (m+n = 4) in different configurations. The first entry in the labels represents the adsorption energy of the cluster (in eV) and the second entry represents the elongation of N2 (in Ao). .The gray, yellow and red balls represent Hf, Ta and N atoms, respectively..Here * denote adsorption of N2 on other atom site.

For HfTa3 (figure 5 fifth row), the bond length of Hf-Ta and Ta-Ta are 2.53 A˚ and 2.39 A˚ respectively. The complete cleavage of bond-length of N-N occurs in '4c' and 4d configurations, whereas cleavage of double bond length of N2 is observed in '4e' and '4e*', and cleavage of triple bond length of N-N are observed in '4b', '4f' and '4f*'. The configuration '4d' has adsorption energy of 3.31 eV for breaking bond length of dinitrogen with 2.58 A˚ completely. So, this configuration '4d' is suitable, however, the configuration '4c' is energetically favorable.

2.4.2 Tetrahedron-shaped

For tertrahedron-shaped tetramers, the N2 adsorbed structures (figure 6 first row). The Hf4 tetramer have Hf-Hf bond length 2.76 A˚. The complete cleavage of bond-length of N-N occurs in '5c', '5d' and '5e' configurations, whereas cleavage of single bond length of N2 is observed in '5a' configuration and cleavage of triple bond-length of N2 is observed in '5b' configuration. '5d' configuration are energetically favorable and '5c' configuration is most favorable for distorted tetrahedron. The equatorial configuration is favorable for cleavage of dinitrogen in hafnium clusters. The Ta4 tetramer has Ta-Ta bond length 2.53 A˚. The N2 adsorbed structures (figure 6 last row). The complete cleavage of bond-length of N-N occurs in '5c', '5d' and '5e' configurations, whereas cleavage of triple bond length of N2 is observed in '5a' and '5b' configurations. '5d' configuration is energetically more favorable and '5c' configuration is most favorable in the sense that less energy is required to dissociate dinitrogen. Here the adsorption energy per atom decreases with increase in bond length of N2 with number of atoms in corresponding configurations well agrees the previous reported studies. The tetrahedron structure is more stable than the square-shaped. The equatorial configuration is favorable for cleavage of dinitrogen in tantalum clusters.

For bimetallic tetramers HfmTan (m+n = 4), the tetramer structure can also be formed with several constituents as discussed above. For Hf3Ta the optimized structures (Figure 6 second row) have bond length Hf-Hf and Hf-Ta as 2.81 A˚ and 2.60 A˚ resp. The complete cleavage of bond-length of N-N occurs in '5a', '5c', '5d' and '5e' configurations, whereas cleavage of second bond length of N2 is observed in '5a*' and cleavage of triple bond length of N-N are observed in '5b' and '5b*'. For Hf2Ta2 the optimized structures (figure 6 third row) have bond length Hf-Hf, Hf-Ta and Ta-Ta as 2.82 A˚, 2.85 A˚ and 2.45 A˚ resp. The complete cleavage of bond-length of N-N occurs in '5c', '5d' and '5e' configurations whereas cleavage of second bond length of N2 are observed in '5a', '5b*' and cleavage of triple bond-length of N-N is observed in '5a*' and '5b' . Configurations '5c' and '5d' are energetically favorable and the configuration '5b' has less adsorption energy. For HfTa3 the optimized structures (Figure 6 fourth row) have bond length Ta-Ta and Hf-Ta as 2.59 A˚ and 2.67 A˚ resp. The complete cleavage of bond-length of N-N occurs in '5c', '5d' and '5e' configurations, whereas cleavage of double bond length of N2 is observed in '5a' and cleavage of triple bond-length of N-N is observed in '5a*', '5b' and '5b*'. Here, '5d' configuration is energetically favorable and the configuration '5a*' has less adsorption energy.

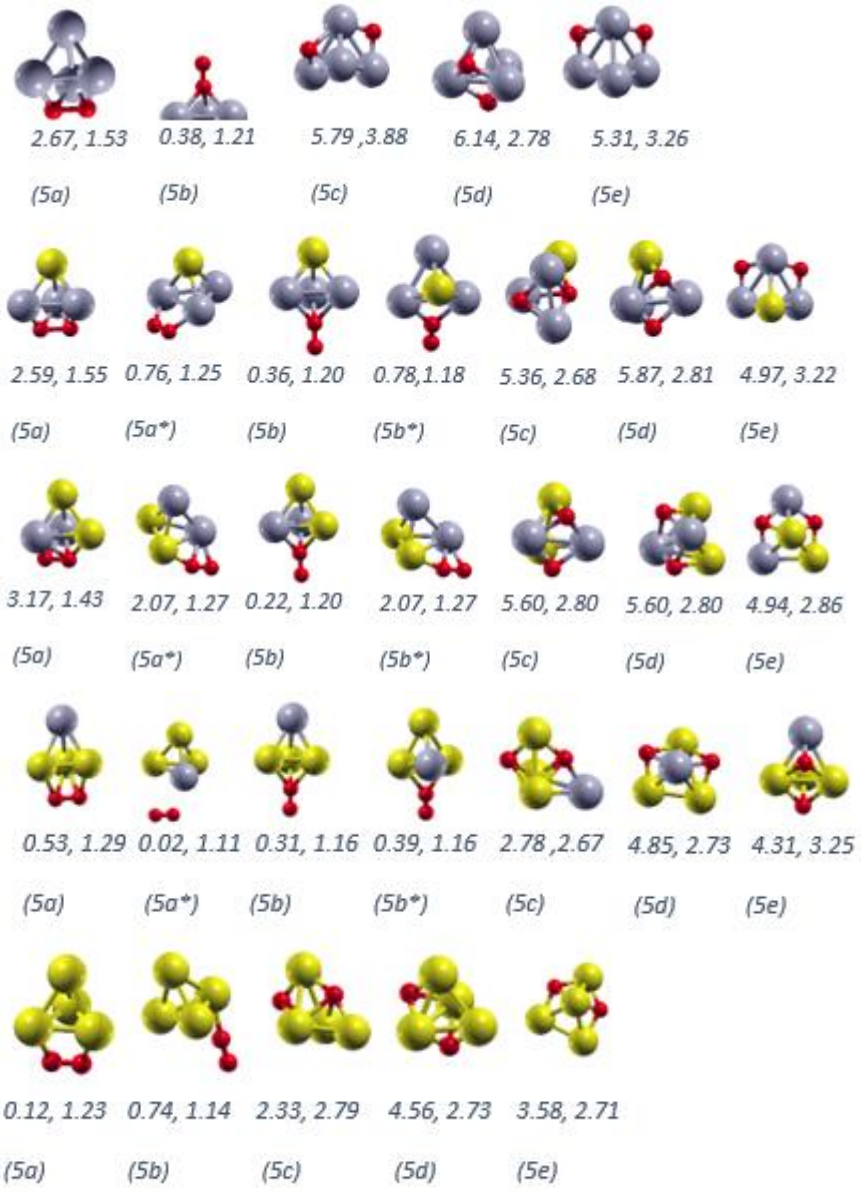


Figure 6. Optimized global minimum structures of HfmTan clusters (m+n = 4) in different configurations. The first entry in the labels represents the adsorption energy of the cluster (in eV) and the second entry represents the elongation of N2 (in Ao). .The gray, yellow and red balls represent Hf, Ta and N atoms, respectively. Here * denote adsorption of N2 on other atom site.

5. Conclusion

The adsorption and dissociation of dinitrogen on mono-metallic and bimetallic clusters of HfmTan clusters (where m+n ≤ 4) have been studied by using DFT based first principles calculations. The dissociation of N-N bond is found to be strongly dependent on orientation of N-N axis with respect to the axis of the adsorbent cluster. Orientation of N-N axis, whether perpendicular or parallel, to cluster axis has been found to be suitable for dissociative adsorption of dinitrogen depending upon geometries and size of clusters. It is found that the adsorption energies of HfmTan clusters differs significantly on varying sizes and configurations. Our Study also shows that even dimer can dissociate dinitrogen completely.

Acknowledgment

This research was supported in part through computational resources provided by the Kathmandu University Supercomputer Centre, which was established with equipment donated by CERN..

References

[1] Huda, M. N., & Kleimann, L. (2006). Hydrogen adsorption and dissociation on small platinum clusters: An electronic structure density functional study, 74, 195407.

[2] Ping, S.L., Gan, L. Y., Tian., R. Y., & Zhao, Y. J. (2011). Theoretical study of CO adsorption and oxidation on the gold–palladium bimetal clusters, 977(1-3), 62-68.

[3] Yadav, M. K., & Mookerjee, A. (2010). Nitrogen absorption and dissociation on small Tantalum clusters, 405(18), 3940-3942.

[4] https://en.wikipedia.org/wiki/Haber process

[5] Roy, D., Vazquez, A. N., & Schleyer, V. R. (2009). Modeling Dinitrogen Activation by Lithium: A Mechanistic Investigation of the Cleavage of N2 by Stepwise Insertion into Small Lithium Clusters. Journal of the American Chemical Society, 131 (36), 13045-13053.

[6] Acharya, R., Pant, N., Jha, V. L., & Yadav, M. K. (2020). Adsorption and dissociation of dinitrogen on mono-metallic and bimetallic clusters. International Journal of Modern Physics B, 34(26), 2050236.

[7] Giannozzi, P et al. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter, 21(39), 395502.

[8] Giannozzi, P et al. (2017). Advanced capabilities for materials modelling with Quantum ESPRESSO. Journal of Physics: Condensed Matter, 29(46), 465901.

[9] Bloch, P. E. (1994). Projector augmented-wave method. Phys. Rev. B 50, 17953.

[10] Kress, G., & Joubert, D. (1994). From ultrasound pseudopotentials to the projector augmented wave method. Physical Review B, 59(3), 1758-1775.

[11] Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. Phyical Review Letters, 78(7), 3865.

[12] Kokalj, A. (2003). Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. Computational Materials Science, 28(2), 155-168.

[13] Grunze, M., Golze, M., Hirchwald, W., Freund, H. F., Pulm, H., Seip, U., Tsai, M. C., Ertl, G., & Kuppers, J. (1984). π-Bonded N2 on Fe(111): The Precursor for Dissociation. Physical Review Letters, 53(8), 850-853.

[14] Jules, J. L., & Lombardi, J. R. (2003). Transition Metal Dimer Internuclear Distances from Measured Force Constants. The journal of Physical Chemistry A, 107(9), 1268-1273.

[15] Zhao, R. N., Han, J. G., & Sheng, L. S. (2012). Geometries, electronic and magnetic properties of hafnium clusters: A density functional calculation, 520, 2178-2183.

[16] Herzberg, G. (1950). Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules.