

Adsorption of small gas molecules on B₃₆ nanocluster

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Abstract. Adsorption of CO, N₂, H₂O, O₂, H₂ and NO molecules on B₃₆ cluster was studied using density functional theory (DFT) with B3LYP functional and 6-311+G(d,p) basis set. Energies, enthalpies and Gibbs free energies of the adsorption processes were calculated. The thermodynamic data showed that the B₃₆ cluster is a good adsorbent only for CO, O₂ and NO molecules. The calculated energies of adsorption of N₂, H₂O and H₂ on the B₃₆ cluster were positive values. CO molecule is adsorbed via the carbon atom more effectively, while the nitrogen atom of NO is adsorbed better than the oxygen atom. Also, when NO and O₂ are adsorbed synchronously via both atoms, they dissociate. The edge boron atoms of the B₃₆ cluster showed more reactivity than the inner atoms.

Keywords. B₃₆ cluster; Adsorption; Density functional theory; Gas molecules.

1. Introduction

Boron (B) has vast applications in science and industry and is used to prepare many compounds such as hard materials, semiconductors, glasses and antitumor medicines.¹ Also, pure clusters of boron can be used as novel ligands.² Many researchers have studied the structural and chemical properties of boron clusters by computational methods and experimental techniques.^{3–8} Small clusters of boron tend to have planar or quasi-planar structures.^{9–13} The π -systems of planar boron clusters have noticeable similarity to those of polycyclic aromatic hydrocarbons, and therefore, concept of aromaticity and anti-aromaticity have been applied for them.^{9–16} Sergeeva *et al.*⁹ have studied structural and chemical properties of anionic B_n (n=3–24) clusters using computational methods and photoelectron spectroscopy. Their results showed that the most stable isomers of anionic boron clusters up to 24 atoms have 2D planar or quasi-planar structures.⁹ Another study on B₁₉[–] cluster showed that B₁₉[–] has a planar structure with a hexagonal central B₆ unit within a B₁₃ ring.¹⁷ Wu *et al.*¹⁸ have performed a theoretical study on the structure and stability of 2D boron monolayer sheets and reported that the most stable structures are α - and β -sheets which have filled hexagonal hole.

There are a few studies on the adsorption of small gases on the boron clusters.^{19,20} Sun *et al.*¹⁹ studied adsorption of H₂, N₂, CH₄ and CO₂ on the B₈₀. They found that only CO₂ molecule forms strong bond with

basic site of B₈₀ and other molecules form weak binding with B₈₀. Also, CO₂ can bond with B₁₂ and B₂₈ due to Lewis acid-base interaction.¹⁰

Boron can form extended single-atom sheets with filled hexagonal hole.^{21,22} The extended sheet is called “borophene” whose units consist of 36 boron atoms. The B₃₆ cluster has both planar and quasi-planar structures. Piazza *et al.*²¹ and Chen *et al.*²² provided the first experimental evidence that the B₃₆ planar boron sheets are viable. They used photoelectron spectroscopy to study the B₃₆ clusters and reported that B₃₆[–] is quasi-planar with central hexagonal hole while neutral B₃₆ is a highly stable cluster with C_{6v} hexagonal symmetry. B₃₆ may find different applications in future. It may be used as adsorbent or catalyst in some reactions. In this work, we study the interaction and adsorption of small molecules including H₂O, NO, CO, H₂, O₂ and N₂ on the neutral B₃₆ cluster.

2. Computational Details

Density functional theory (DFT) with B3LYP functional was used to optimize the structures of B₃₆ clusters, the B₃₆-molecule complexes of CO, N₂, NO, H₂, O₂ and H₂O. The calculations were performed using 6-311+G(d,p) basis set which involves polarization and diffuse functions. Frequency calculations were performed at the same level of theory to obtain the thermodynamic properties of the optimized structures. The thermal energy is obtained from the results of the frequency calculations, ($E_{\text{Thermal}} = E_{\text{vib}} + E_{\text{rot}} + E_{\text{tran}}$) at

*For correspondence

298.15 K. Enthalpy (H) and Gibbs free energy are calculated as $H = E_{\text{Thermal}} + E_{\text{ele}} + RT$ and $G = H - TS$, where E_{ele} is electronic energy. Equilibrium constant (K_{eq}) for planar \leftrightarrow quasi-planar was calculated using $\Delta G = -RT \ln K_{\text{eq}}$ at 298.15 K. Zero point vibrational energies (ZPE) and thermal corrections were considered in order to obtain the energy values (E, H and G). Gaussian 09 quantum chemistry package was used in all calculations.²³

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their energies were determined using canonical method in Gaussian 09.²³ Mulliken charge distributions were calculated employing B3LYP/6-311+G(d,p) method.

The adsorption energies (E_{ads}) of CO, NO, N₂, H₂, O₂ and H₂O on B₃₆ were calculated from eq. 1:

$$E_{\text{ads}} = E_{\text{B}_{36}\text{-gas}} - (E_{\text{B}_{36}} + E_{\text{gas}}) \quad (1)$$

where $E_{\text{B}_{36}\text{-gas}}$ is the total energy of complex of B₃₆ with adsorbed gas, $E_{\text{B}_{36}}$ is the energy of the isolated B₃₆ cluster, and E_{gas} is the energy of the isolated gas molecules (CO, NO, N₂, H₂, O₂ and H₂O). The adsorption enthalpies (ΔH_{ads}) and Gibbs free energies (ΔG_{ads}) were calculated with the same method at 298.15 K

Electronegativities (χ) of the studied compounds were computed by the following equation²⁴

$$\chi = -\frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \quad (2)$$

3. Results and Discussion

3.1 Planar and Quasi-planar B₃₆ Cluster

The B₃₆ cluster is a single-atom thick boron cluster which has both planar (D_{6h}) and quasi-planar (C_{6v})

structures.^{21,22} Figure 1 shows the planar and quasi-planar forms of the B₃₆ cluster optimized at B3LYP level. Geometric parameters of both the structures have been collected in Supplementary Information (figure S1). The B-B bond lengths are different in the two isomers. Piazza *et al.*²¹ optimized the structure of C_{6v} isomer by PBE0 method and reported two B-B bond length (1.67 and 1.58 Å) for edge atoms. These bond lengths are in good agreement with our results obtained by B3LYP method. Mulliken charge distributions of the planar and quasi-planar isomers are different. Boron atoms of two internal rows in the planar isomer have positive partial charges and edge atoms have negative charges. Charge distribution in the C_{6v} isomer is not regular so that six internal boron atoms are positively charged while boron atoms in the middle and edge rows have both positive and negative charges. Also, the enthalpy (ΔH) and Gibbs free energy (ΔG) of the D_{6h} \leftrightarrow C_{6v} (planar \leftrightarrow quasi-planar) inter-conversion were calculated by B3LYP method (figure 1). The quasi-planar structure is more stable than the planar structure. The calculated equilibrium constant (K_{eq}) for the C_{6v} \leftrightarrow D_{6h} inter-conversion shows that relative abundance of the quasi-planar structure is about 10¹⁰ times that of the planar form. Furthermore, entropy of the quasi-planar form (C_{6v}) is larger than that for planar isomer (D_{6h}) at 298.15 K ($\Delta S = +58.96 \text{ J/mol.K}$) which is reasonable.

3.2 Adsorption of CO on the B₃₆ Cluster

The planar structure of B₃₆ was used as adsorbent in this study. However, in some cases, the planar adsorbent was converted to the quasi-planar form due to interaction with the gas molecules. Mostly, the planar cluster

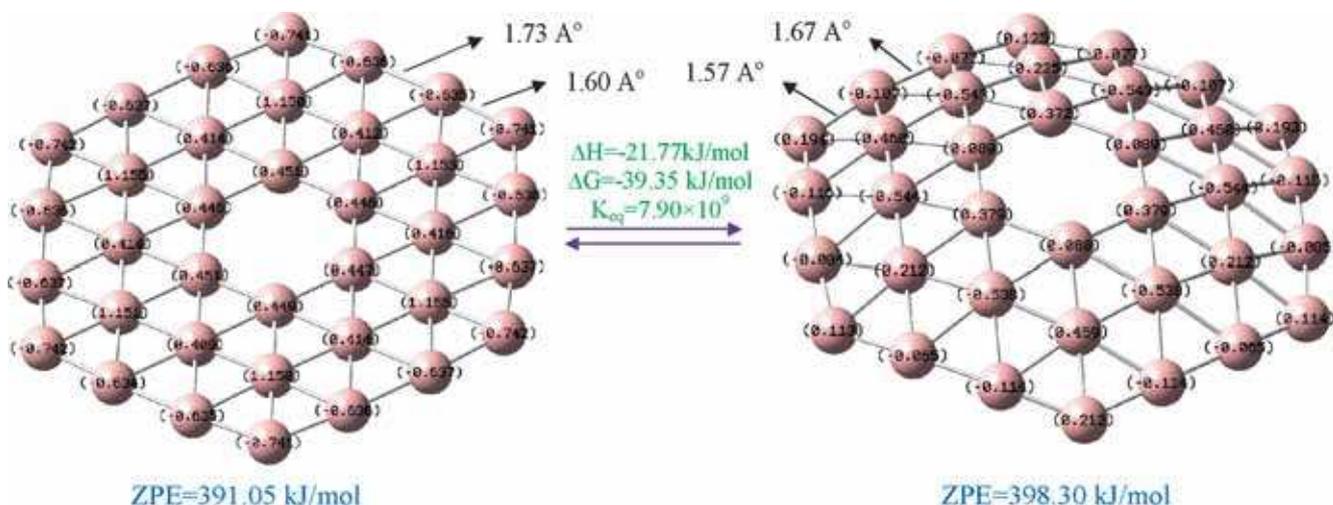


Figure 1. The planar and quasi-planar structures of the B₃₆ cluster optimized at B3LYP level of theory.

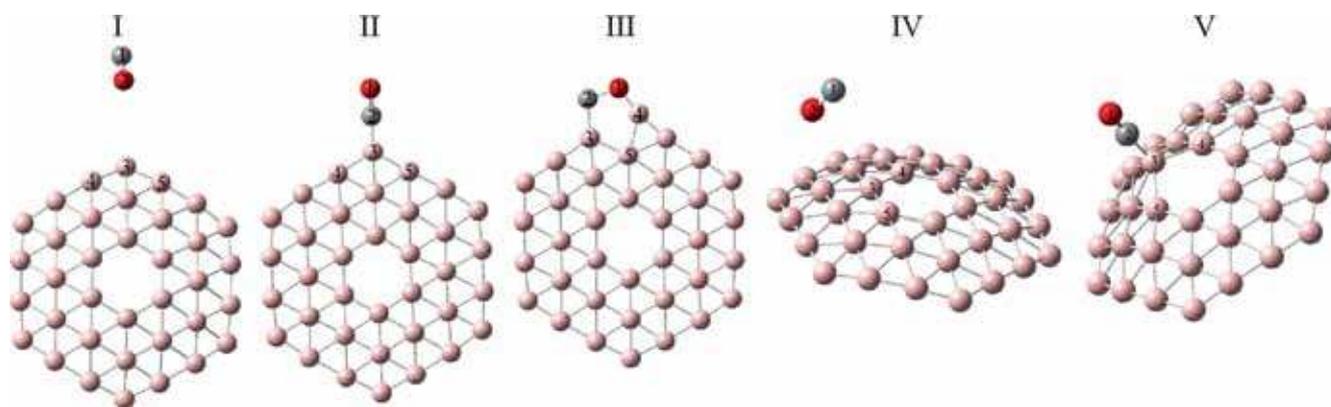


Figure 2. The optimized structures of different types of adsorption of CO on the B₃₆ cluster. The oxygen and carbon atoms are in red and grey colors, respectively, and numbering of the atoms is used to determine the geometrical parameters.

maintained its structure in the chemical adsorption when the bonds formed and the cluster are on the same surface. In other words, the orbitals of planar isomer have more suitable orientation than those of the quasi-planar isomer to form chemical bonds with the molecules. Figure 2 shows five types of interactions of CO with the B₃₆ cluster. As seen, the planar B₃₆ cluster converts to the quasi-planar form in Types I, IV and V after interaction with CO molecule. Figure 2 shows that CO adsorbs on the B₃₆ cluster generally via its carbon atom. Boron atom has five electrons, therefore its p orbital is partially empty. The charge distribution of atoms in the Type II showed that the Mulliken charge of the boron atom 3 which is bonded with the carbon atom of CO is -2.02 that indicates the boron atom has accepted a lone pair from the CO. For charge distributions of all adsorption systems see Supplementary Information (figure S2).

The energies (E_{ads}), enthalpies (ΔH_{ads}) and Gibbs free energies (ΔG_{ads}) of adsorption of CO on the B₃₆ cluster were calculated at 298 K using eq. 1 (table 1).

The “ZPE correction” in the parenthesis indicates that the energy values have been corrected for the zero point vibrational energy (ZPE). Also, some of the important geometrical parameters of B₃₆-CO complexes have been tabulated in table 1. The complete geometrical parameters can be found in Supplementary Information (figure S1). $E_{\text{B}_{36}}$ in eq. 1 is the energy of the isolated B₃₆ cluster. However, the B₃₆ cluster has two structures, planar and quasi-planar. Since we studied adsorption of the gases on the planar isomer and its distortion is due to interaction with the gas molecules, $E_{\text{B}_{36}}$ was considered as the energy of the planar isomer for all calculations. When CO was kept with its oxygen atom in the vicinity and in the plane of the B₃₆ cluster, the chemical adsorption did not occur (Type I). The same result was observed in the case of Type IV. The inter cluster separation of CO and B₃₆ (B-O) in the Type I and IV are 3.94 and 4.30 Å, respectively. These lengths are longer than a normal chemical bond.²⁵ The calculated enthalpies of adsorption for Types I and IV are about -2 kJ/mol which confirm that CO has been weakly adsorbed.

Table 1. The calculated thermodynamic and structural data for adsorption of CO on the B₃₆ cluster (see figure 2). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	I	II	III	IV	V
E_{ads} (kJ/mol)	+1.10	-50.44	+146.21	+0.89	+21.92
E_{ads} (ZPE corrected)	+0.40	-42.78	+147.64	-0.10	+37.36
ΔH_{ads} (kJ/mol)	-1.37	-52.92	+143.73	-1.58	+19.46
ΔH_{ads} (ZPE corrected)	-2.00	-45.26	+145.16	-2.58	+34.89
ΔG_{ads} (kJ/mol)	+18.63	-9.59	+188.43	+26.21	+47.52
ΔG_{ads} (ZPE corrected)	+18.01	-1.93	+189.87	+25.21	+62.95
r_{12}	1.127	1.141	1.364	1.127	1.136
r_{23}	3.944	1.471	1.641	4.302	1.532
r_{14}	5.963	3.796	1.366	5.714	3.692
Angle 123	176.34	179.99	105.74	111.90	172.01
Angle 234	116.71	121.03	66.97	121.97	111.89
Angle 235	115.90	121.03	117.51	90.10	112.04

Furthermore, the C-O bond length of CO in isolated CO and in Types I and IV are the same (1.127 Å) indicating physisorption. In the Type II, CO is chemically adsorbed from the carbon atom. The bond length of C-O (r_{12}) and C-B (r_{23}) are 1.141 and 1.471 Å, respectively. Also, the enthalpy of adsorption for Type II is about -50 kJ/mol indicating a chemical adsorption. The calculated adsorption energies for the Type III and V are positive. In the Type III, CO adsorbed on the B₃₆ from both carbon and oxygen atoms. Although two chemical bonds are formed in Type III, the adsorption energies are positive because the C-O bond becomes weaker ($r_{12}=1.364$ Å), a B-B bond is broken and the B₃₆ structure is disturbed. The ΔG_{ads} values at 298 K are more positive than the ΔH_{ads} , probably due to difference in the entropies of the gas molecules before and after adsorption. The entropies of the gas molecules decrease after adsorption.

3.3 Adsorption of N₂ on the B₃₆ Cluster

Figure 3 shows the interaction of N₂ with the B₃₆ cluster. In the Type VI and VII, N₂ molecule was put in the vicinity of edge B atoms and in the plane of B₃₆ cluster, and then the systems were optimized using B3LYP method. The optimized structures showed that N₂ adsorbs on the B₃₆ cluster through edge boron atoms. On the other hand, when N₂ molecule was put on top of the plane of the B₃₆ cluster, it did not adsorb on the surface (Type VIII). The charge distribution results of Type VI showed that the N and B atoms in the N-B bond have partial charges of +0.05 and -0.55, respectively. Since B has electron deficiency, it shares some of the negative charge of the nitrogen electrons. The same discussion is applicable for the Type VII. For complete charge distribution analysis see Supplementary Information (figure S2).

Table 2 summarizes the calculated values of E_{ads} , ΔH_{ads} and ΔG_{ads} for the adsorption of N₂ on the B₃₆ cluster. Also, important geometrical parameters of

Table 2. The calculated thermodynamic and structural data for adsorption of N₂ on the B₃₆ cluster (see figure 3). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	VI	VII	VIII
E_{ads} (kJ/mol)	+51.40	+165.12	+2.75
E_{ads} (ZPE corrected)	+58.16	+168.40	+3.77
ΔH_{ads} (kJ/mol)	+48.93	+162.64	+0.27
ΔH_{ads} (ZPE corrected)	+55.69	+165.92	+1.29
ΔG_{ads} (kJ/mol)	+92.57	+203.68	+17.80
ΔG_{ads} (ZPE corrected)	+99.34	+206.96	+18.82
r_{12}	1.113	1.297	1.095
r_{23}	1.471	1.449	4.257
r_{14}	3.753	1.353	5.618
Angle 123	179.99	114.79	166.03
Angle 234	121.04	61.44	94.21
Angle 235	121.04	113.05	100.21

B₃₆-N₂ complexes have been tabulated in table 2. The complete geometrical parameters have been collected in Supplementary Information (figure S1). Although figure 3 shows that in the Types VI and VII, N₂ adsorbs on the B₃₆ cluster via chemical bonds, the calculated adsorption energies indicate that the adsorption processes are not thermodynamically favorable. All of the energies of N₂ adsorption are positive. The bond length of N≡N in isolated N₂ is about 1.095 Å while this strong triple bond is somewhat broken and becomes longer in the Types VI and VII (1.113 and 1.297 Å, respectively). It seems the formed B-N bond is not so strong to compensate the breakage of triple bond of N₂. Furthermore, some of the B-B bonds of B₃₆ in the Type VII are broken which are endothermic processes.

3.4 Adsorption of H₂O on the B₃₆ Cluster

Figure 4 shows the interaction of water molecule with B₃₆ cluster. The optimized structures show that water molecule adsorbs via the oxygen atom on an edge B atom when the water and B₃₆ cluster are in the same

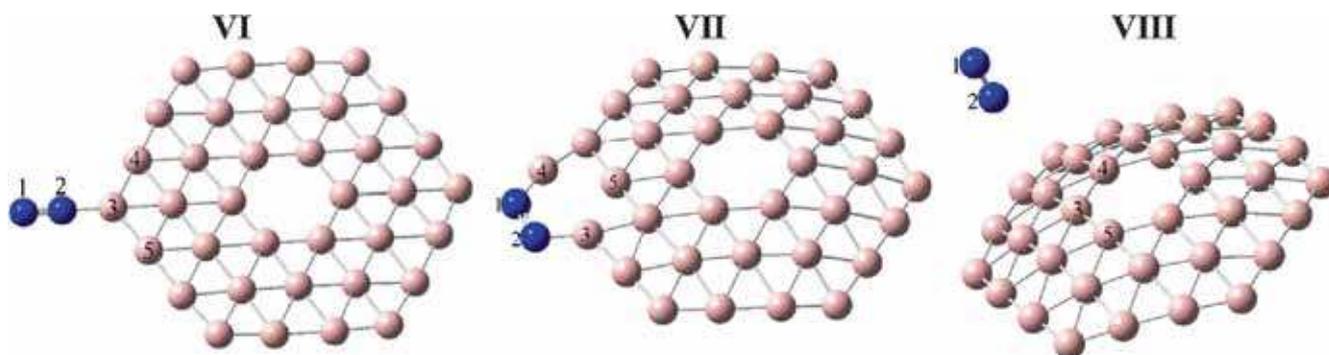


Figure 3. The optimized structures for different types of interaction of N₂ with the B₃₆ cluster.

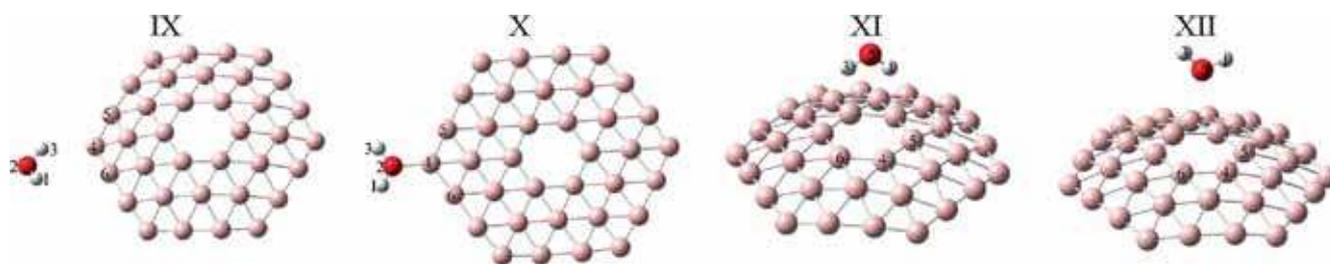


Figure 4. The optimized structures for different types of interaction of H₂O with the B₃₆ cluster.

plane (Type X). In other types (Types IX, XI and XII), the H₂O-B₃₆ distances are longer than 3.5 Å which indicates that these interactions are physisorption.²⁵ The optimized structures show that H₂O adsorbs only on edge boron atoms of the B₃₆ cluster.

Table 3 summarizes the calculated values of E_{ads} , ΔH_{ads} and ΔG_{ads} for the adsorption of H₂O on the B₃₆ cluster. Also, some of the important geometrical parameters of B₃₆-H₂O complexes have been tabulated in table 3. The complete geometrical parameters have been brought together in Supplementary Information (figure S1).

Adsorption of H₂O on the B₃₆ cluster in the Type X is an exothermic reaction ($\Delta H_{\text{ads}} < 0$). The bond length of O-B (r_{24}) in the Type X is 1.58 Å which is about a chemical bond and the three atoms of H₂O are in the plane of the B₃₆ cluster. The H-O-H angle (123) in the B₃₆-H₂O system is about 115° that is larger than that in isolated H₂O molecule. Increase in the H-O-H angle may be due to reduction of lone pair-bond pair repulsion. In the Type XII, although the O-B inter nuclear separation is 3.88 Å and it is a physisorption, the process is an exothermic reaction ($\Delta H_{\text{ads}} < 0$). The oxygen atom of H₂O has partial negative charge (−0.57) which interacts with the six central boron atoms of the B₃₆ cluster.

Table 3. The calculated thermodynamic and structural data for adsorption of H₂O on the B₃₆ cluster (see figure 4). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	IX	X	XI	XII
E_{ads} (kJ/mol)	+1.52	−9.31	+2.38	−2.86
E_{ads} (ZPE corrected)	+3.86	−0.80	+4.16	+0.38
ΔH_{ads} (kJ/mol)	−0.96	−11.79	−0.09	−5.34
ΔH_{ads} (ZPE corrected)	+1.38	−3.28	+1.68	−2.09
ΔG_{ads} (kJ/mol)	+22.83	+33.98	+25.86	+27.49
ΔG_{ads} (ZPE corrected)	+25.17	+42.49	+27.63	+30.73
r_{12}	0.963	0.971	0.962	0.962
r_{24}	3.498	1.589	4.103	3.884
Angle 123	104.48	115.72	104.74	104.78
Angle 124	57.19	122.13	44.49	103.86
Angle 245	117.04	119.87	83.44	78.17
Angle 546	127.59	120.26	119.99	119.98

3.5 Adsorption of NO on the B₃₆ Cluster

Figure 5 shows the interaction of NO with the B₃₆ cluster. It seems that the adsorption of NO on the B₃₆ takes place more easily than other gas molecules. NO adsorbs on the edge boron atoms of B₃₆ cluster via both N and O atoms (Types XIII and XIV). In the Type XV, the N and O atoms synchronously adsorb on the two edge boron atoms of the B₃₆ cluster. The adsorption process in the Type XV is a dissociative adsorption in which the N-O bond is broken. In the Types XIII, XIV and XV, NO molecule and the B₃₆ cluster are in the same plane. Also, adsorption of NO from the top of the B₃₆ surface was investigated (Types XVI and XVII). The optimized structures show that NO molecule does not adsorb on the top of the B₃₆ cluster through only N or O atom. However, when both N and O atoms of NO are involved, the adsorption occurs from the top of the B₃₆ cluster (Types XVII).

The calculated values of E_{ads} , ΔH_{ads} and ΔG_{ads} for the adsorption of NO on the B₃₆ cluster at 298 K have been tabulated in table 4. Also, table 4 summarizes some of the important geometrical parameters of B₃₆-NO complexes. The complete geometrical parameters have been collected in Supplementary Information (figure S1). In the Types XIII and XIV, NO molecule adsorbs on the edge boron atoms via N and O atoms, respectively. However, the adsorption process in the Type XIII is exothermic ($\Delta H_{\text{ads}} < 0$) while the adsorption reaction in the Type XIV is an endothermic process ($\Delta H_{\text{ads}} < 0$). NO molecule is a free radical and its unpaired electron is on the N atom in the Lewis structure. NO molecule coordinates with metal atoms as a ligand generally through its N atom.²⁶ In the adsorption of NO via N atom, the unpaired electron of NO is shared with the B atom and a chemical bond ($r_{12} = 1.33$ Å) is formed (Type XIII). In the Type XIV, the N-O bond is somewhat dissociated ($r_{12} = 1.29$ Å) and formation of O-B bond ($r_{23} = 1.41$ Å) is not too exothermic to recompense it. NO adsorption in the Type XV is a dissociative adsorption in which the O and N atoms independently adsorb on the two boron atoms of the B₃₆ cluster. The bond lengths of N-B (r_{23}) and O-B (r_{14})

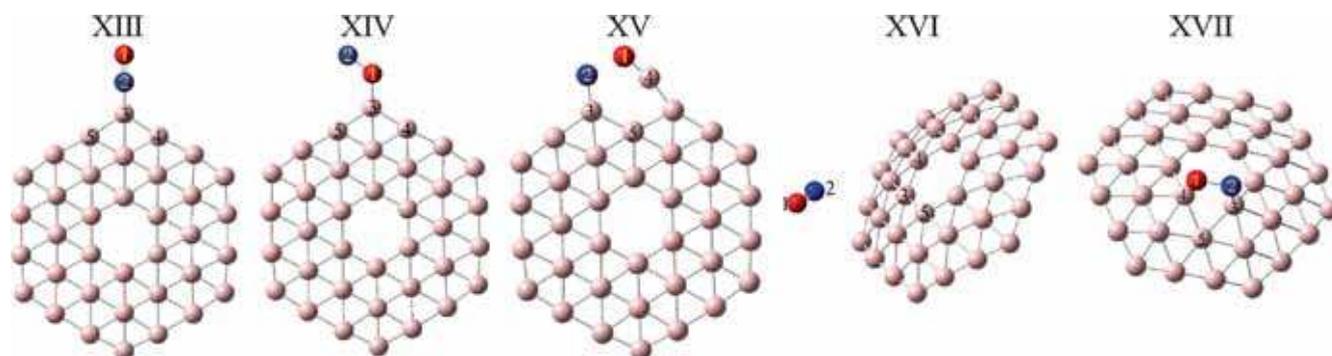


Figure 5. The optimized structures of different types of adsorption of NO on the B_{36} cluster. The O and N atoms are numbered by 1 and 2, respectively.

Table 4. The calculated thermodynamic and structural data for adsorption of NO on the B_{36} cluster (see figure 5). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	XIII	XIV	XV	XVI	XVII
E_{ads} (kJ/mol)	-39.41	+25.71	-175.76	+1.24	-11.02
E_{ads} (ZPE corrected)	-35.35	+24.69	-173.62	+1.30	+2.09
ΔH_{ads} (kJ/mol)	-41.81	+23.23	-178.23	-1.23	-13.50
ΔH_{ads} (ZPE corrected)	-37.76	+22.21	-176.10	-1.17	-0.38
ΔG_{ads} (kJ/mol)	+4.58	+65.78	-133.35	+24.59	+21.52
ΔG_{ads} (ZPE corrected)	+8.64	+64.76	-131.21	+24.65	+34.64
r_{12}	1.170	1.293	1.590	1.147	1.391
r_{23}	1.339	2.406	1.387	3.867	1.508
r_{14}	3.766	2.731	1.268	4.690	1.444
Angle 123	179.99	125.56	110.23	118.64	100.71
Angle 234	123.21	120.11	66.81	110.78	77.13
Angle 235	123.21	126.01	122.73	109.62	109.99

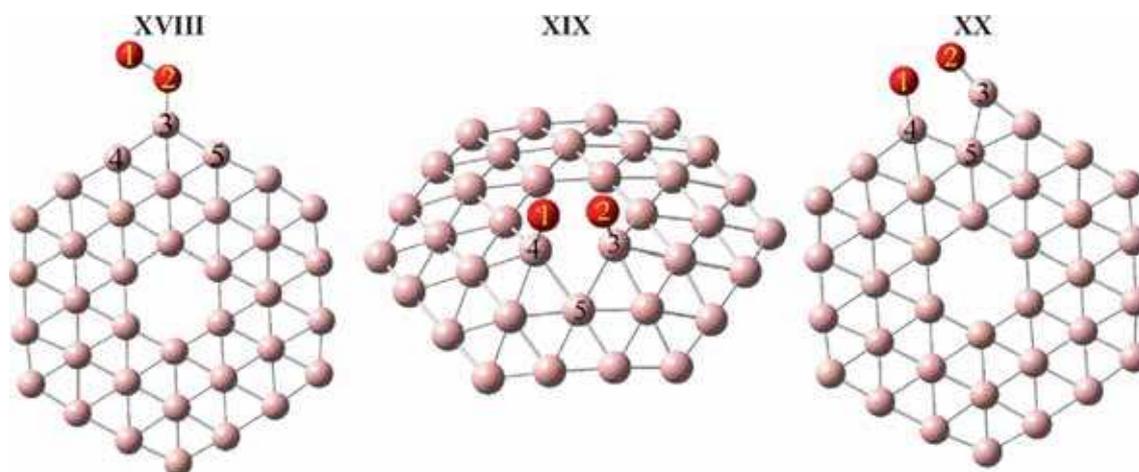


Figure 6. The optimized structures of three different types of adsorption of O_2 on the B_{36} cluster.

are 1.38 and 1.26 Å, respectively, indicating that they are chemical bonds. The dissociative adsorption of NO on the B_{36} cluster is thermodynamically favored and its enthalpy and Gibbs free energy are negative. In the Type XVI, NO molecule was put top of the B_{36} cluster

from N atom. After optimization, it was observed that NO did not adsorb on the B_{36} cluster via only one atom. Instead, when NO molecule was put on the B_{36} cluster and both N and O atoms were involved, the adsorption occurred (Type XVII). The adsorption process in the

Table 5. The calculated thermodynamic and structural data for adsorption of O₂ on the B₃₆ cluster (figure 6). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	XVIII	XIX	XX
E _{ads} (kJ/mol)	-0.52	-145.48	-292.22
E _{ads} (ZPE corrected)	+1.36	-131.66	-284.47
ΔH _{ads} (kJ/mol)	-3.00	-147.96	-294.70
ΔH _{ads} (ZPE corrected)	-1.11	-134.14	-286.95
ΔG _{ads} (kJ/mol)	+42.19	-112.27	-251.94
ΔG _{ads} (ZPE corrected)	+43.99	-98.45	-244.19
r ₁₂	1.335	1.484	1.475
r ₂₃	1.371	1.435	1.355
r ₁₄	3.110	1.436	1.385
Angle 123	120.12	99.87	104.63
Angle 234	127.31	80.15	75.59
Angle 235	118.55	110.19	125.86

Type XVII was exothermic ($\Delta H_{\text{ads}} < 0$), however, due to decrease in NO entropy during the adsorption, ΔG_{ads} of the adsorption was a positive value. In the Types XV and XVII, NO adsorbs via both N and O atoms, but dissociation occurs only in the Type XV. Also, the bond lengths of N-B and O-B in the Type XV are shorter and consequently stronger than those in the Type XVII. Our results show that capability of the edge boron atoms of the B₃₆ cluster to react with NO molecule is more than that of the inner boron atoms. This trend was observed for other gas molecules, so that they adsorb on the edge boron atoms more effectively than on the inside ones.

The calculation showed that the B₃₆ cluster is a capable substrate for adsorption of CO and NO molecules. CO and NO_x, known atmospheric pollutants, are partially produced during combustion of fuels.²⁷ Therefore, significant attempts have been made to remove these chemicals from lean-burn engines and diesel exhaust

fluids.^{27,28} The results of this work show that the B₃₆ can be used as catalyst to adsorb or dissociate the emitted NO and CO from diesel engine. Haber-Bosch process is the main industrial procedure for production of ammonia, from N₂ and H₂. N₂ is very non-reactive due its strong triple bond and large amount energy is required to dissociate this bond. Therefore, Fe is used as catalyst to overcome this barrier energy in the Haber-Bosch process.²⁹ Although adsorption of N₂ on the B₃₆ is endothermic, the N≡N bond is weakened after its adsorption on the B₃₆ cluster. Therefore, B₃₆ cluster may find some applications in the catalytic processes such as ammonia production, in future.

3.6 Adsorption of O₂ on the B₃₆ Cluster

Figure 6 shows the optimum structures for three types of adsorption of O₂ on B₃₆. O₂ can be adsorbed on B₃₆ through one or two oxygen atoms. The O-B bonds are 1.37, 1.43 and 1.36 Å in the Types XVIII, XIX and XX, respectively. These short bonds indicate that the three types are chemical adsorption. The O-O bond of oxygen is weakened or broken after adsorption so that it is 1.33, 1.48 and 1.47 Å in the Type XVIII, XIX and XX, respectively which are larger than O-O bond of free oxygen (1.20 Å). In other words, in the Types XIX and XX in which O₂ adsorbs via the two oxygen atoms, the O-O bond dissociation occurs, too.

Table 5 summarizes the calculated values of E_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption of O₂ on B₃₆ at 298 K. Thermodynamic data of adsorption of oxygen on B₃₆ depend on how adsorption takes place. For the Types XIX and XX, in which O₂ adsorbs via both oxygen atoms the adsorption processes are strongly exothermic and the ΔH_{ads} values are about -140 and -290 kJ/mol, respectively. Although dissociation of the O-O bond in

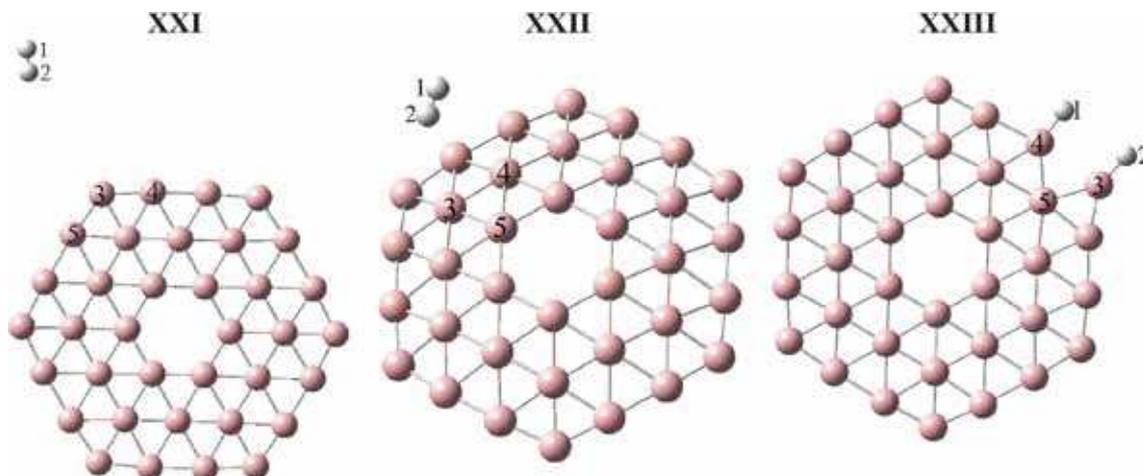


Figure 7. The optimized structures of three different types of adsorption of H₂ on the B₃₆ cluster.

Table 6. The calculated thermodynamic and structural data for adsorption of H₂ on the B₃₆ cluster (figure 7). The energies, bond lengths (r) and angles are in kJ/mol, Angstrom and degree, respectively.

	XXI	XXII	XXIII
E _{ads} (kJ/mol)	-6.11	-32.99	-65.81
E _{ads} (ZPE corrected)	-6.03	-27.27	-49.62
ΔH _{ads} (kJ/mol)	-8.59	-35.46	-68.28
ΔH _{ads} (ZPE corrected)	-8.51	-29.74	-52.09
ΔG _{ads} (kJ/mol)	+30.07	-30.43	-36.71
ΔG _{ads} (ZPE corrected)	+30.86	-24.71	-20.52
r ₁₂	0.744	0.743	2.252
r ₂₃	5.448	4.550	1.168
r ₁₄	6.912	4.825	1.176
Angle 123	155.43	125.67	82.67
Angle 234	115.59	79.03	97.80
Angle 235	116.89	76.31	149.63

the Types XIX and XX is endothermic (ΔH_{ads} > 0), formation of two strong B-O bonds releases much amount energy so that the total process is an exothermic reaction (ΔH_{ads} < 0). On the other hand, when O₂ adsorbs through only one of its atoms, the formation of the B-O bond compensates the O=O rupture. Therefore, the ΔH_{ads} and E_{ads} values are about zero (Type XVIII).

3.7 Adsorption of H₂ on the B₃₆ Cluster

Figure 7 shows the optimum structures for three types of adsorption of H₂ on B₃₆. In the Type XXI, H₂ interacts with the edge boron atoms only via one hydrogen atom which does not lead to formation of a chemical bond between H and B atoms because the H-B inter nuclear separation is about 5.4 Å. Furthermore, H₂ does not adsorb on atop of B₃₆ (Type XXII) and the H-B inter nuclear separation is about 4.5 Å. On the other hand, H₂ is adsorbed via both hydrogen atoms on the edge boron atoms of B₃₆ (Type XXIII). The lengths of the formed H-B bonds are about 1.16 Å which implies that the process is a chemical adsorption.^{24,25} Also, in the Type XXIII the H-H bond was dissociated after adsorption so that its length became 2.25 Å which is very much longer than that of the free H₂ molecule (0.74 Å).

Table 6 summarizes the calculated values of E_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption of H₂ on B₃₆ at 298 K. The interactions in the three types are exothermic adsorption (ΔH_{ads} < 0). Although interaction in the Types XXII is physisorption, it has considerable adsorption energy. The main part of the released energy in the Type XXII is due to conversion of B₃₆ cluster from planar to quasi-planar form (figure 1). The energy

Table 7. Comparison of adsorption energies (E_{ads}), HOMO-LUMO gap energies, electronegativities (χ) and equilibrium distances (R) of B₃₆-gas molecules.

Compound	R (Å)	E _{ads} (kJ/mol)	E _{HOMO} -E _{LUMO} (eV)	χ (eV)
Planar-B ₃₆			2.06	4.93
Quasi-planar-B ₃₆			1.88	4.89
Type-I	3.94 (O-B)	+1.10	1.88	4.88
Type-II	1.47 (C-B)	-50.44	1.73	5.06
Type-III	1.36 (O-B)	+146.21	1.43	5.15
Type-IV	4.00 (O-B)	+0.89	1.88	4.89
Type-V	1.53 (C-B)	+21.92	1.51	4.99
Type-VI	1.47 (N-B)	+51.40	1.75	4.99
Type-VII	1.35 (N-B)	+165.12	1.15	5.12
Type-VIII	4.25 (N-B)	+2.75	1.88	4.88
Type-IX	3.08 (H-B)	+1.52	1.88	5.01
Type-X	1.58 (O-B)	-9.31	2.05	4.47
Type-XI	3.40 (H-B)	+2.38	1.87	5.00
Type-XII	3.88 (O-B)	-2.86	1.88	4.76
Type-XIII	1.34 (N-B)	-39.41	1.49	4.82
Type-XIV	1.41 (O-B)	+25.71	1.13	5.06
Type-XV	1.38 (N-B)	-175.76	1.58	4.94
Type-XVI	3.44 (N-B)	+1.24	1.87	4.88
Type-XVII	1.44 (O-B)	-11.02	1.23	4.95
Type-XVIII	1.37 (O-B)	-0.52	1.22	5.65
Type-XIX	1.43 (O-B)	-145.48	1.19	5.32
Type-XX	1.36 (O-B)	-292.22	1.83	4.89
Type-XXI	5.44 (H-B)	-6.11	2.06	4.93
Type-XXII	4.55 (H-B)	-32.99	1.88	4.89
Type-XXIII	1.16 (H-B)	-65.81	1.95	4.85

of dissociative adsorption of H₂ (Type XIII) is about 65 kJ/mol which is more than those for the Types XXI and XII.

We have not reported any entropy value (ΔS) for the adsorption of the gas molecules on the B₃₆ cluster. The ΔS values can be calculated from the equation $\Delta G = \Delta H - T\Delta S$ at 298 K. The reported data in tables 1-6 show that the entropy values decrease during the adsorption process.

Table 7 compares adsorption energies (E_{ads}), HOMO-LUMO gap energies, electronegativities (χ) and equilibrium distances (R) of B₃₆-molecule complexes. The HOMO-LUMO gap energy of quasi-planar form of B₃₆ is 1.88 eV. The HOMO-LUMO gap energies after the physisorption are about 1.88 eV which are equal to that of quasi-planar B₃₆. For the systems in which chemical bonds are formed between gas molecules and B₃₆, the HOMO-LUMO gap energies are generally less than that for B₃₆ (<1.88 eV). The electronegativities of the systems in which the interaction is physical adsorption (R > 2 Å) are the same as that of the quasi-planar B₃₆ (4.89 eV). On the other hand, in the systems with chemical adsorption the electronegativities change and are different from that of B₃₆. It seems the HOMO-LUMO gap energies and electronegativities depend on adsorption nature (chemical or physical) and R rather than adsorption energies.

4. Conclusion

The B₃₆ cluster has both planar and quasi-planar structures whose quasi-planar form is more stable. Adsorption of six molecules, CO, N₂, H₂O, O₂, H₂ and NO on the planar B₃₆ cluster was studied. The calculations showed that when the molecule adsorbs chemically on the B₃₆ cluster, it maintains the planar structure. Furthermore, in the cases that the interaction between the gas molecules and B₃₆ is physisorption, the interaction causes conversion of the B₃₆ cluster from planar to the quasi-planar structure. CO, O₂ and NO are adsorbed on B₃₆ more effectively through formation chemical bonds. Also, CO and NO are adsorbed on the B₃₆ cluster via the C and N atoms. When NO and O₂ molecules are adsorbed via both their atoms, the N-O and O-O bonds are broken (dissociative adsorption). Our calculations showed that the outer (edge) boron atoms at the end of the B₃₆ cluster adsorb the gas molecule better than the inner boron atoms.

Supplementary Information

All additional information pertaining to geometrical parameters of the compounds and their charge

distribution analysis (figures S1, S2) are given in the supporting information available at www.ias.ac.in/chemsci.

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