J. Chem. Sci. Vol. 127, No. 11, November 2015, pp. 2029–2038. © Indian Academy of Sciences.
DOI 10.1007/s12039-015-0967-y

Adsorption of small gas molecules on B_{36} nanocluster

YOUNES VALADBEIGI*, HOSSEIN FARROKHPOUR and MAHMOUD TABRIZCHI
Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Iran
e-mail: y.valadbeigi@ch.iut.ac.ir

MS received 8 May 2015; revised 3 September 2015; accepted 7 September 2015

Abstract. Adsorption of CO, N_2, H_2O, O_2, H_2 and NO molecules on B_{36} 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 B_{36} cluster is a good adsorbent only for CO, O_2 and NO molecules. The calculated energies of adsorption of N_2, H_2O and H_2 on the B_{36} 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 O_2 are adsorbed synchronously via both atoms, they dissociate. The edge boron atoms of the B_{36} cluster showed more reactivity than the inner atoms.

Keywords. B_{36} 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 B_{19}^- cluster showed that B_{19}^- has a planar structure with a hexagonal central B_6 unit within a B_{13} 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 H_2, N_2, CH_4 and CO_2 on the B_{80}. They found that only CO_2 molecule forms strong bond with basic site of B_{80} and other molecules form weak binding with B_{80}. Also, CO_2 can bond with B_{12} and B_{28} 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 B_{36} cluster has both planar and quasi-planar structures. Piazza *et al.*[21] and Chen *et al.*[22] provided the first experimental evidence that the B_{36} planar boron sheets are viable. They used photoelectron spectroscopy to study the B_{36} clusters and reported that B_{36}^- is quasi-planar with central hexagonal hole while neutral B_{36} is a highly stable cluster with C_{6v} hexagonal symmetry. B_{36} 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 H_2O, NO, CO, H_2, O_2 and N_2 on the neutral B_{36} cluster.

2. Computational Details

Density functional theory (DFT) with B3LYP functional was used to optimize the structures of B_{36} clusters, the B_{36}-molecule complexes of CO, N_2, NO, H_2, O_2 and H_2O. 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, ($E_{Thermal} = E_{vib} + E_{rot} + E_{tran}$) at

*For correspondence

298.15 K. Enthalpy (H) and Gibbs free energy are calculated as $H = E_{Thermal} + E_{ele} + RT$ and G=H-TS, where E_{ele} is electronic energy. Equilibrium constant (K_{eq}) for planar↔qusi-planar was calculated using $\Delta G = -RT\ln K_{eq}$ 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, N_2, H_2, O_2 and H_2O on B_{36} were calculated from eq. 1:

$$E_{ads} = E_{B36-gas} - \left(E_{B36} + E_{gas}\right) \quad (1)$$

where $E_{B36-gas}$ is the total energy of complex of B_{36} with adsorbed gas, E_{B36} is the energy of the isolated B_{36} cluster, and E_{gas} is the energy of the isolated gas molecules (CO, NO, N_2, H_2, O_2 and H_2O). 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 equation[24]

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

3. Results and Discussion

3.1 *Planar and Quasi-planar B_{36} Cluster*

The B_{36} 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 B_{36} 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 PBEO 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}↔C_{6v} (planar↔quasi-planer) 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}↔D_{6h} inter-conversion shows that relative abundance of the quasi-planar structure is about 10^{10} 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 ($\Delta S = +58.96 J/mol.K$) which is reasonable.

3.2 *Adsorption of CO on the B_{36} Cluster*

The planar structure of B_{36} 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

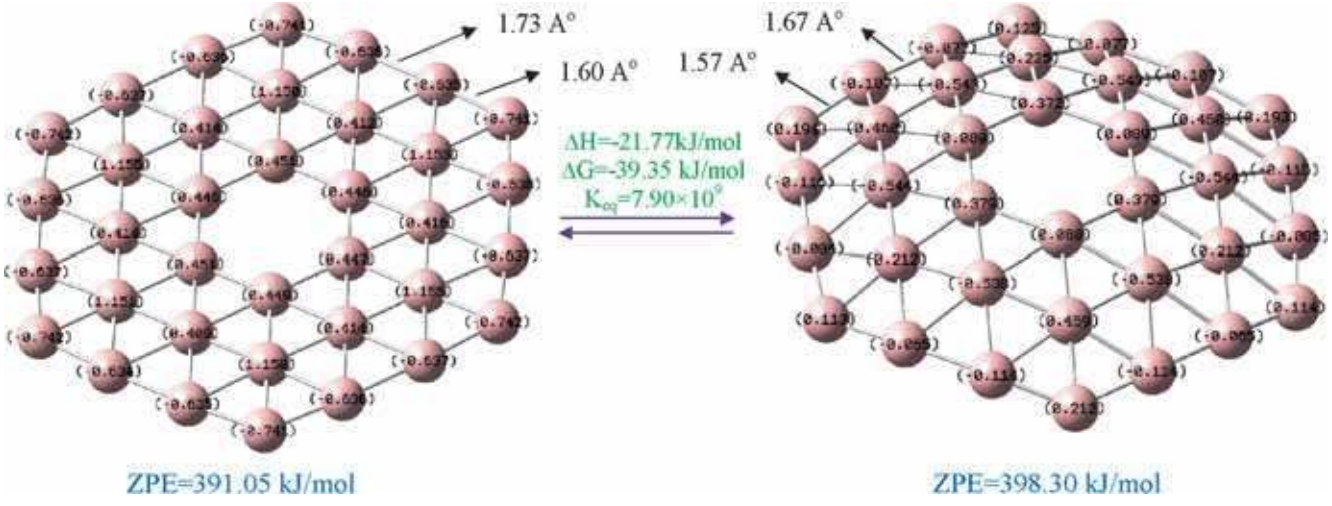

Figure 1. The planar and quasi-planar structures of the B_{36} cluster optimized at B3LYP level of theory.

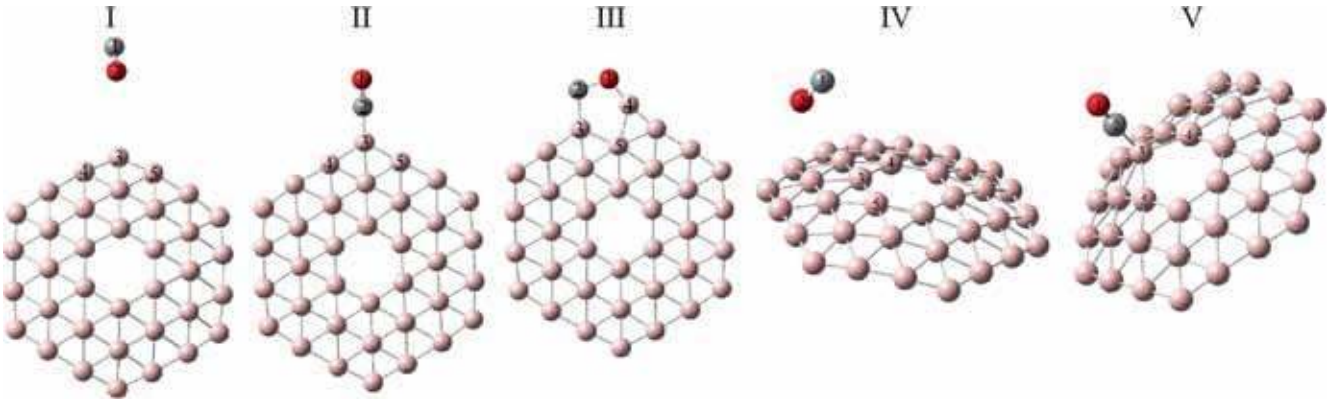

Figure 2. The optimized structures of different types of adsorption of CO on the B_{36} cluster. The oxygen and carbon atoms are in red and grey colors, respectively, and numbering of the atoms is used to determine the geometrical parameters.

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 B_{36} cluster. As seen, the planar B_{36} 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 B_{36} 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 B_{36} 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 B_{36}-CO complexes have been tabulated in table 1. The complete geometrical parameters can be found in Supplementary Information (figure S1). E_{B36} in eq. 1 is the energy of the isolated B_{36} cluster. However, the B_{36} 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_{B36} 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 B_{36} 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 B_{36} (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 B_{36} 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 B_{36} 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 B_{36} 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 N_2 on the B_{36} Cluster*

Figure 3 shows the interaction of N_2 with the B_{36} cluster. In the Type VI and VII, N_2 molecule was put in the vicinity of edge B atoms and in the plane of B_{36} cluster, and then the systems were optimized using B3LYP method. The optimized structures showed that N_2 adsorbs on the B_{36} cluster through edge boron atoms. On the other hand, when N_2 molecule was put on top of the plane of the B_{36} 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 N_2 on the B_{36} cluster. Also, important geometrical parameters of

Table 2. The calculated thermodynamic and structural data for adsorption of N_2 on the B_{36} 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

B_{36}-N_2 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, N_2 adsorbs on the B_{36} cluster via chemical bonds, the calculated adsorption energies indicate that the adsorption processes are not thermodynamically favorable. All of the energies of N_2 adsorption are positive. The bond length of N≡N in isolated N_2 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 N_2. Furthermore, some of the B-B bonds of B_{36} in the Type VII are broken which are endothermic processes.

3.4 *Adsorption of H_2O on the B_{36} Cluster*

Figure 4 shows the interaction of water molecule with B_{36} cluster. The optimized structures show that water molecule adsorbs via the oxygen atom on an edge B atom when the water and B_{36} cluster are in the same

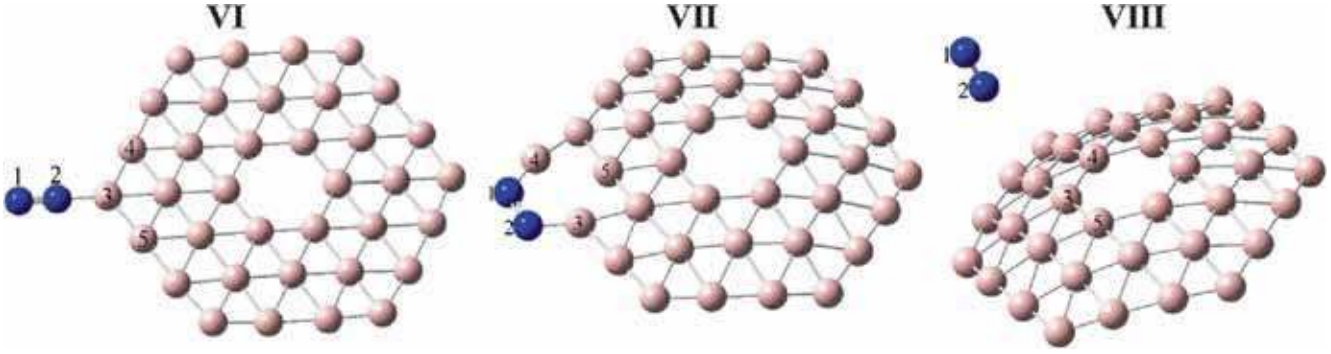

Figure 3. The optimized structures for different types of interaction of N_2 with the B_{36} cluster.

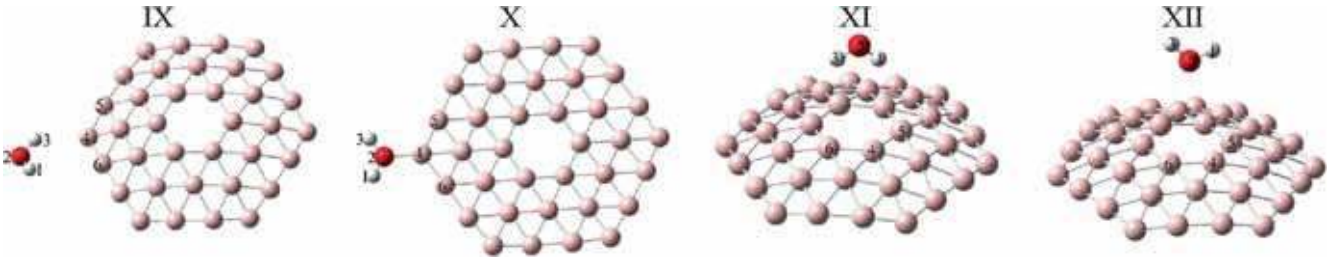

Figure 4. The optimized structures for different types of interaction of H_2O with the B_{36} cluster.

plane (Type X). In other types (Types IX, XI and XII), the H_2O-B_{36} distances are longer than 3.5 Å which indicates that these interactions are physisorption.[25] The optimized structures show that H_2O adsorbs only on edge boron atoms of the B_{36} cluster.

Table 3 summarizes the calculated values of E_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption of H_2O on the B_{36} cluster. Also, some of the important geometrical parameters of B_{36}-H_2O complexes have been tabulated in table 3. The complete geometrical parameters have been brought together in Supplementary Information (figure S1).

Adsorption of H_2O on the B_{36} cluster in the Type X is an exothermic reaction (ΔH_{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 H_2O are in the plane of the B_{36} cluster. The H-O-H angle (123) in the B_{36}-H_2O system is about 115° that is larger than that in isolated H_2O 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 (ΔH_{ads} <0). The oxygen atom of H_2O has partial negative charge (−0.57) which interacts with the six central boron atoms of the B_{36} cluster.

Table 3. The calculated thermodynamic and structural data for adsorption of H_2O on the B_{36} 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 B_{36} Cluster*

Figure 5 shows the interaction of NO with the B_{36} cluster. It seems that the adsorption of NO on the B_{36} takes place more easily than other gas molecules. NO adsorbs on the edge boron atoms of B_{36} 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 B_{36} 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 B_{36} cluster are in the same plane. Also, adsorption of NO from the top of the B_{36} surface was investigated (Types XVI and XVII). The optimized structures show that NO molecule does not adsorb on the top of the B_{36} 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 B_{36} cluster (Types XVII).

The calculated values of E_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption of NO on the B_{36} cluster at 298 K have been tabulated in table 4. Also, table 4 summarizes some of the important geometrical parameters of B_{36}-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 (ΔH_{ads}<0) while the adsorption reaction in the Type XIV is an endothermic process (ΔH_{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 B_{36} cluster. The bond lengths of N-B (r_{23}) and O-B (r_{14})

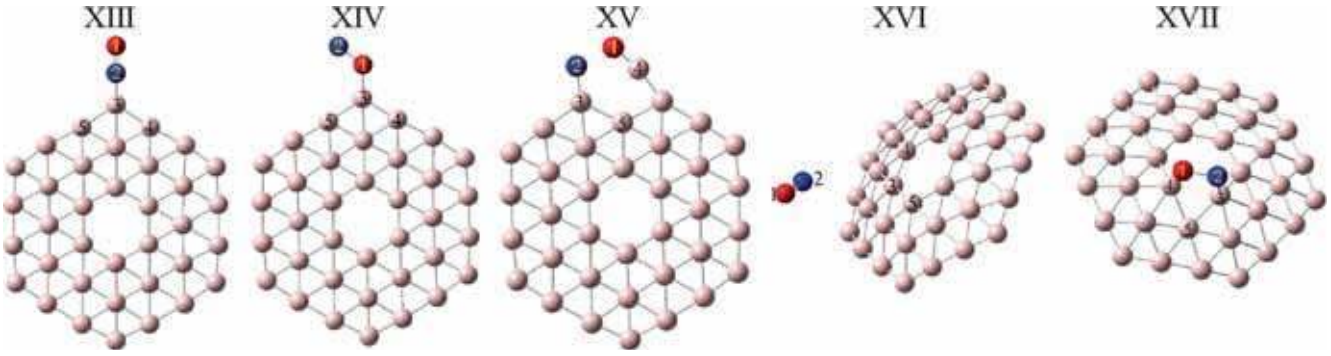

Figure 5. The optimized structures of different types of adsorption of NO on the B_{36} cluster. The O and N atoms are numbered by 1 and 2, respectively.

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

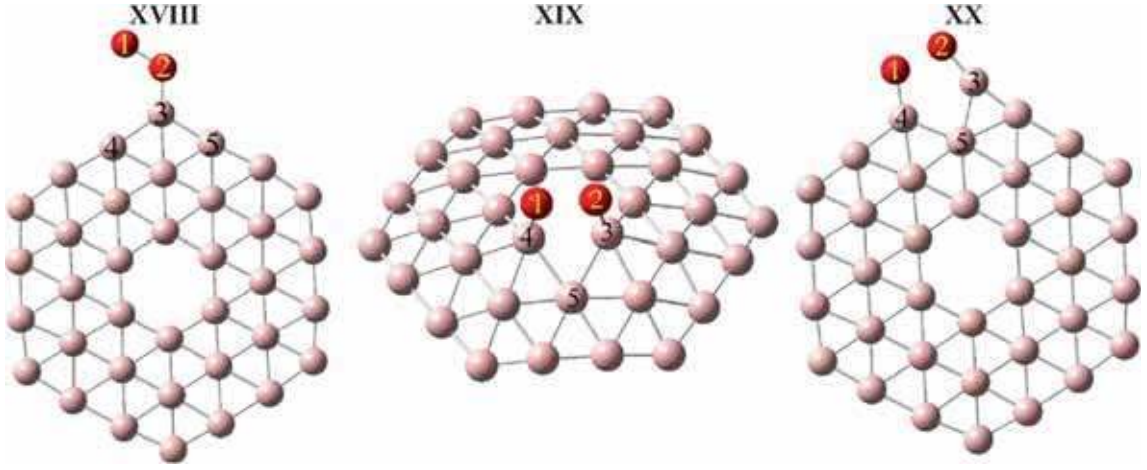

Figure 6. The optimized structures of three different types of adsorption of O_2 on the B_{36} cluster.

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 O_2 on the B_{36} 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 ($\Delta H_{ads} < 0$), 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 B_{36} 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 B_{36} 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 B_{36} 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 N_2 and H_2. N_2 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 N_2 on the B_{36} is endothermic, the N≡N bond is weakened after its adsorption on the B_{36} cluster. Therefore, B_{36} cluster may find some applications in the catalytic processes such as ammonia production, in future.

3.6 *Adsorption of O_2 on the B_{36} Cluster*

Figure 6 shows the optimum structures for three types of adsorption of O_2 on B_{36}. O_2 can be adsorbed on B_{36} 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 O_2 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 O_2 on B_{36} at 298 K. Thermodynamic data of adsorption of oxygen on B_{36} depend on how adsorption takes place. For the Types XIX and XX, in which O_2 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

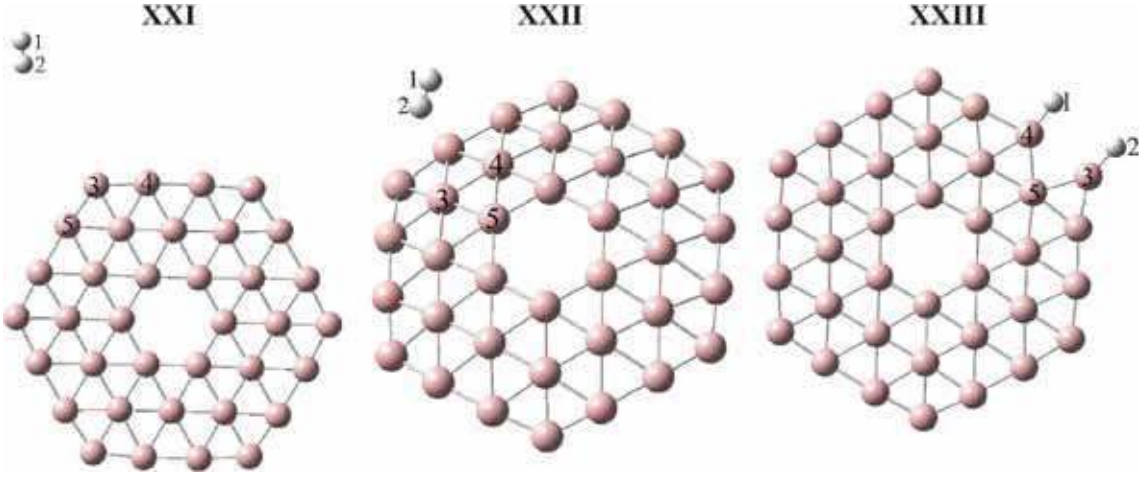

Figure 7. The optimized structures of three different types of adsorption of H_2 on the B_{36} cluster.

Table 6. The calculated thermodynamic and structural data for adsorption of H_2 on the B_{36} 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 ($\Delta H_{ads} > 0$), formation of two strong B-O bonds releases much amount energy so that the total process is an exothermic reaction ($\Delta H_{ads} < 0$). On the other hand, when O_2 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 H_2 on the B_{36} Cluster*

Figure 7 shows the optimum structures for three types of adsorption of H_2 on B_{36}. In the Type XXI, H_2 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, H_2 does not adsorb on atop of B_{36} (Type XXII) and the H-B inter nuclear separation is about 4.5 Å. On the other hand, H_2 is adsorbed via both hydrogen atoms on the edge boron atoms of B_{36} (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 H_2 molecule (0.74 Å).

Table 6 summarizes the calculated values of E_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption of H_2 on B_{36} at 298 K. The interactions in the three types are exothermic adsorption ($\Delta H_{ads} < 0$). 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 B_{36} 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 B_{36}-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 H_2 (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 B_{36} 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 B_{36}-molecule complexes. The HOMO-LUMO gap energy of quasi-planar form of B_{36} 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 B_{36}. For the systems in which chemical bonds are formed between gas molecules and B_{36}, the HOMO-LUMO gap energies are generally less than that for B_{36} (<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 B_{36} (4.89 eV). On the other hand, in the systems with chemical adsorption the electronagativities change and are different from that of B_{36}. 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 B_{36} cluster has both planar and quasi-planar structures whose quasi-planar form is more stable. Adsorption of six molecules, CO, N_2, H_2O, O_2, H_2 and NO on the planar B_{36} cluster was studied. The calculations showed that when the molecule adsorbs chemically on the B_{36} cluster, it maintains the planar structure. Furthermore, in the cases that the interaction between the gas molecules and B_{36} is physisorption, the interaction causes conversion of the B_{36} cluster from planar to the quasi-planar structure. CO, O_2 and NO are adsorbed on B_{36} more effectively through formation chemical bonds. Also, CO and NO are adsorbed on the B_{36} cluster via the C and N atoms. When NO and O_2 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 B_{36} 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.

Acknowledgment

The authors wish to express thanks to the Center of Excellency in Chemistry of Isfahan University of Technology.

References

1. Alexandrova A N, Boldyrev A I, Zhai H J and Wang L S 2006 *Coord. Chem. Rev.* **250** 2811
2. Li S D, Guo J C, Miao C Q and Ren G M 2005 *Angew. Chem. Int. Ed.* **44** 2158
3. Chen Q, Zhang S Y, Bai H, Tian W J, Gao T, Li H R, Miao C Q, Mu Y W, Lu H G, Zhai H J and Li S D 2015 *Angew. Chem. Int. Ed.* **54** 8160
4. Xu J, Chan Y, Gan L, Ma Y and Zhai T 2015 *Adv. Sci.* **2**. doi: doi: 10.1002/advs.201500023
5. Prasad D L V K and Jemmis E D 2008 *Phys. Rev. Lett.* **100** 165504
6. Zhai H J, Zhao Y F, Li W L, Chen Q, Bai H, Hu H S, Piazza Z A, Tian W J, Lu H G, Wu Y B, Mu Y W, We G F, Liu Z P, Li J, Li S D and Wang L S 1999 *Nat. Chem.* **6** 727
7. Szwacki N G, Sadrzadeh A and Yakobson B I 2008 *Phys. Rev. Lett.* **98** 166804
8. Boustani I, Quandt A, Hernandez E and Rubio A 1999 *J. Chem. Phys.* **110** 3176
9. Sergeeva A P, Popov I A, Piazza Z A, Li W L, Romanescu C, Wang L S and Boldyrev A I 2014 *Acc. Chem. Res.* **47** 1349
10. Galeev T R, Chen Q, Guo J C, Bai H, Miao C Q, Lu H G, Sergeeva A P, Li S D and Boldyrevn A I 2011 *Phys. Chem. Chem. Phys.* **13** 11575
11. Piazza Z A, Li W L, Romanescu C, Sergeeva A P, Wang L S and Boldyrev A 2012 *J. Chem. Phys.* **136** 104310
12. Yang X, Ding Y and Ni J 2008 *Phys. Rev. B* **77** 041402 (R)
13. Tang H and Ismail-Beigi S 2007 *Phys. Rev. Lett.* **99** 115501
14. Sergeeva A P, Zubarev D Y, Zhai H J, Boldyrev A I and Wang L S 2008 *J. Am. Chem. Soc.* **130** 7244
15. Zhai H J, Kiran B, Li J and Wang L S 2003 *Nat. Mater.* **2** 827
16. Sergeeva A P, Piazza Z A, Romanescu C, Li W L and Boldyrev A I 2012 *J. Am. Chem. Soc.* **134** 18065
17. Huang W, Sergeeva A P, Zhai H J, Averkiev B B, Wang L S and Boldyrev A I 2010 *Nat. Chem.* **2** 202
18. Wu X, Dai J, Zhao Y, Zhao Z, Yang J and Zeng X C 2012 *ACS Nano* **6** 7443
19. Sun Q, Wang M, Li Z, Du A and Searles D J 2014 *J. Phys. Chem. C* **118** 2170
20. Sun Q, Wang M, Li Z, Du A and Searles D J 2014 *Phys. Chem. Chem. Phys.* **16** 12695
21. Piazza Z A, Hu H S, Li W L, Zhao Y F, Li J and Wang L S 2014 *Nat. Commun.* **5** 3113
22. Chen Q, Wei G F, Tian W J, Bai H, Liu Z P, Zhai H J and Li S D 2014 *Phys. Chem. Chem. Phys.* **16** 18282

23. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J A, Jr., Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas O, Foresman J B, Ortiz J V, Cioslowski J and Fox D J 2009 *Gaussian 09, Revision A.1*. (Wallingford: Gaussian, Inc.)
24. Nojini Z B and Samiee S 2011 *J. Phys. Chem. C* **115** 12054
25. Rafati A A, Hashemianzadeh S M and Nojini Z B 2008 *J. Phys. Chem. C* **112** 3597
26. Crabtree R H 2005 In *The Organometallic Chemistry of Transition Metals* (New York: John Wiley)
27. Fujitani T, Nakamura L, Kobayashi Y, Takahashi I, Haneda M and Hamada H 2005 *J. Phys. Chem. B* **109** 17603
28. Machida M, Ikeda S, Kurogi D and Kijima T 2001 *Appl. Catal. A* **35** 107
29. Ertl G, Lee S B and Weiss M 1982 *Surf. Sci.* **114** 515