STRUCTURES AND PROPERTIES OF $VB_5^{-/0}$ CLUSTERS FROM DENSITY FUNCTIONAL THEORY CALCULATIONS

Tran Van Tan[1], Ngo Thi Phuoc An[2], Tran Thanh Tuan[3], Nguyen Thi Hong Hanh[1], Nguyen Minh Thao[1], Tran Quoc Tri[1], and Nguyen Hoang Lin[4*]
[1]Dong Thap University, Vietnam
[2]To Ong Vang Primary School, Dong Thap province, Vietnam
[3]Tan Hiep High School, Kien Giang province, Vietnam
[4]Mai Thanh The High School, Soc Trang province, Vietnam
[*]Corresponding author: Nguyen Hoang Lin, Email: nguyenhoanglin.c3mtt@soctrang.edu.vn

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Abstract

Density functional theory with the BPW91 functional and def2-TZVP basis sets was used to investigate the geometric structures of $VB_5^{-/0}$ clusters. By using the bee colony algorithm, 300 initial structures are created for the studied cluster. The geometry optimizations at the BPW91/def2-SVP level result in 18 low-lying isomers in quartet states for the anionic cluster. The results at the BPW91/def2-TZVP level show relative energies and vibrational frequencies for different spin states of 7 isomers of the anionic clusters and 6 isomers of the neutral cluster. It is found that the most stable isomers are A-$VB_5^{-/0}$ with non-planar pentagonal structure. The adiabatic detachment energy of the anionic cluster and the ionization energy of the neutral cluster are 1.93 and 7.36 eV.

Keywords: *BPW91 functional, electron detachment energy, geometric structure, ionization energy, $VB_5^{-/0}$ clusters.*

CẤU TRÚC VÀ TÍNH CHẤT CỦA CLUSTER $VB_5^{-/0}$ TÍNH BẰNG LÝ THUYẾT PHIẾM HÀM MẬT ĐỘ

Trần Văn Tân[1], Ngô Thị Phước An[2], Trần Thanh Tuấn[3], Nguyễn Thị Hồng Hạnh[1], Nguyễn Minh Thảo[1], Trần Quốc Trị[1] và Nguyễn Hoàng Lin[4*]
[1]Trường Đại học Đồng Tháp, Việt Nam
[2]Trường Tiểu học Tổ Ong Vàng, tỉnh Đồng Tháp, , Việt Nam
[3]Trường Trung học phổ thông Tân Hiệp, tỉnh Kiên Giang, Việt Nam
[4]Trường Trung học phổ thông Mai Thanh Thế, tỉnh Sóc Trăng, Việt Nam
[*]Tác giả liên hệ: Nguyễn Hoàng Lin, Email: nguyenhoanglin.c3mtt@soctrang.edu.vn

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Tóm tắt

Lý thuyết phiếm hàm mật độ với phiếm hàm BPW91 và bộ hàm cơ sở def2-TZVP được sử dụng để nghiên cứu cấu trúc hình học của cluster $VB_5^{-/0}$. Bằng cách sử dụng thuật toán đàn ong nhân tạo, 300 cấu trúc ban đầu được tạo ra cho cluster được nghiên cứu. Quá trình tối ưu hóa hình học bằng phiếm hàm BPW91 và bộ hàm cơ sở def2-SVP cho thấy cluster anion có 18 đồng phân năng lượng thấp ở trạng thái quartet. Phiếm hàm BPW91 và bộ hàm cơ sở def2-TZVP cũng tính được năng lượng tương đối và tần số dao động điều hòa ứng với trạng thái spin khác nhau của 7 đồng phân của cluster anion và 6 đồng phân của cluster trung hòa. Kết quả tính toán cho thấy rằng đồng phân bền nhất là A-$VB_5^{-/0}$ với cấu trúc ngũ giác không phẳng. Năng lượng tách của cluster anion và năng lượng ion hóa của cluster trung hòa là 1,93 và 7,36 eV.

Từ khóa: *Phiếm hàm BPW91, năng lượng tách electron, cấu trúc hình học, năng lượng ion hóa, cluster $VB_5^{-/0}$.*

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1. Introduction

Clusters of transition metal with boron have been extensively investigated because of their potential application in catalysis and nanomaterial (Demirci et al., 2016; Mananghaya et al., 2016; Zhang et al., 2017). Several clusters of transition metals with boron such as MnB_{16}^{-} and RbB_{18}^{-} are highly stable and can be used as fundamental building-blocks for nanomaterial (Jian et al., 2916a; Jian et al., 2016b). On the other hand, methane has been known as an important resource which can be used to synthesize high value compounds (Guo et al., 2014; Zhou et al., 2019). However, the σ C-H bond of methane is very stable with bond dissociation energy of 440 kJ/mol (Karakaya & Kee, 2016). Therefore, catalysts should be employed to activate the C-H bond of methane. In order to search for the efficient catalysts, the reactivity of VB_{n}^{+} (n=3-6) clusters with methane were investigated by mass spectroscopy (Chen et al., 2018). From the mass spectra, the products of the reactions of VB_3^+, VB_4^+, VB_5^+, and VB6+ clusters with methane are determined to be $VB_3CH_2^+ + H_2$ and $B_3CH_3 + VH^+$; $VB_4CH_2^+ + H_2$ and $B_4CH_4 + V^+$; $VB_5CH_2^+$; and $VB_6CH_2^+$ and $VB_6CH_4(CH_2)_n^+$ (n = 0-2). Density functional theory with M06L and BPW91 functionals were applied to establish mechanisms for the reactions of VB_3^+, VB_4^+, and VB_5^+ clusters with methane (Chen et al., 2018; Tran et al., 2020; Tran & Tran, 2019). It was found that the formation of products is thermodynamically and kinetically favorable. These experimental and theoretical results provide new insight into the designation of new catalysts for methane activation.

Although the structures of the cationic VB_5^+ clusters and mechanism of this cluster with methane were studied, the geometric structures and energetic properties of the anionic and neutral $VB_5^{-/0}$ clusters have not been reported (Tran et al., 2020). This study applied density functional theory to search for the low-lying isomers of $VB_5^{-/0}$ clusters. The BPW91 functional were employed for the studied system because this functional proves to be sufficient to study the structures of VB_4^+ and VB_5^+ (Tran et al., 2020; Tran & Tran, 2019). The geometries, spin states, vibrational frequencies and normal modes, relative energies, electron detachment energies of the anionic cluster, and ionization energies of the neutral cluster were calculated. The computational results gave a clear understanding of the geometrical structures of $VB_5^{-/0}$ clusters.

2. Computational Methods

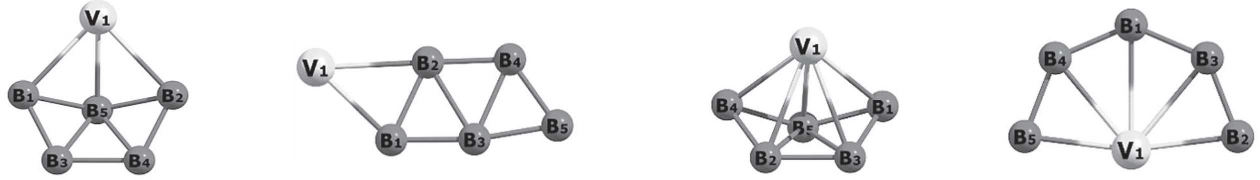
Density functional theory was carried out to investigate the geometric structures of $VB_5^{-/0}$ clusters. The BPW91 functional was chosen for these studied systems because this functional proves to be appropriate to study the $VB_4^{0/+}$ clusters (Tran & Tran, 2019). All the density functional theory calculations were executed with NWCHEM 6.8 package (Valiev et al., 2010). The geometry optimization and vibrational frequency calculations were performed for all the possible spin states to search for the relevant isomers. To search for the important structures of the studied clusters, the artificial bee colony algorithm as implemented in ABCluster package was utilized (Zhang & Dolg, 2015). The initial 300 structures as generated with the artificial bee colony algorithm were optimized with the BPW91 functional (Becke, 1988) and def2-SVP basis sets(Weigend & Ahlrich, 2005). Then, the geometry optimization and vibrational frequency calculations were performed with def2-TZVP basis sets (Weigend, F. and Ahlrichs R., 2005) to improve the energies. The atomic charges of the relevant isomers were calculated by doing natural population analysis (NPA) with JANPA package (Nikolaienko et al., 2014).

3. Results and Discussion

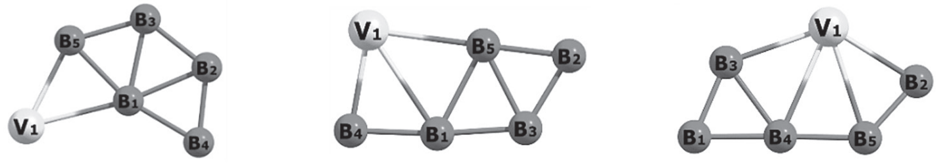
3.1. VB_5^-

The geometry optimizations of 300

structures created by the bee colony algorithm with the BPW91 functional and def2-SVP basis sets for the quartet states of VB_5^- cluster resulted in 18 structures with relative energies from 0.00 to around 2.00 eV. Based on these 18 initial structures, geometry optimizations and vibrational frequency calculations were performed for the doublet, quartet, and sextet states. The structures, spin multiplicities, relative energies, and vibrational frequency of the doublet, quartet, and sextet states of 7 important isomers of VB_5^- as computed at the BPW91/def2-TZVP level are presented in Figure 1 and Table 1. The results show that all the structures belong to the minima on the potential surface because all the vibrational frequencies are positive. The most stable isomer is A-VB_5^- with a non-planar pentagonal structure in which the V atom locates at a corner of the pentagon. The ground state of A-VB_5^- is the doublet; the quartet is just 0.10 eV above; and the sextet is 0.69 eV less stable. The second isomer is labeled as B-VB_5^- with relative energies of the quartet, sextet, and doublet states of 0.42, 0.46, and 0.51 eV. This isomer has planar structure in which the V atom directly binds to two boron atoms of a trapezoidal B_5 moiety. The C-VB_5^- in quartet state is higher in energy than the anionic ground state by 0.50 eV. The remaining 4 isomers are less stable than the first isomer by at least 0.60 eV.



A–VB_5^-, 2, 0.00 **B–VB_5^-, 4, 0.42** **C–VB_5^-, 4, 0.50** **D–VB_5^-, 4, 0.60**



E–VB_5^- , 6, 0.63 **F–VB_5^-, 4, 0.76** **G–VB_5^-, 4, 0.82**

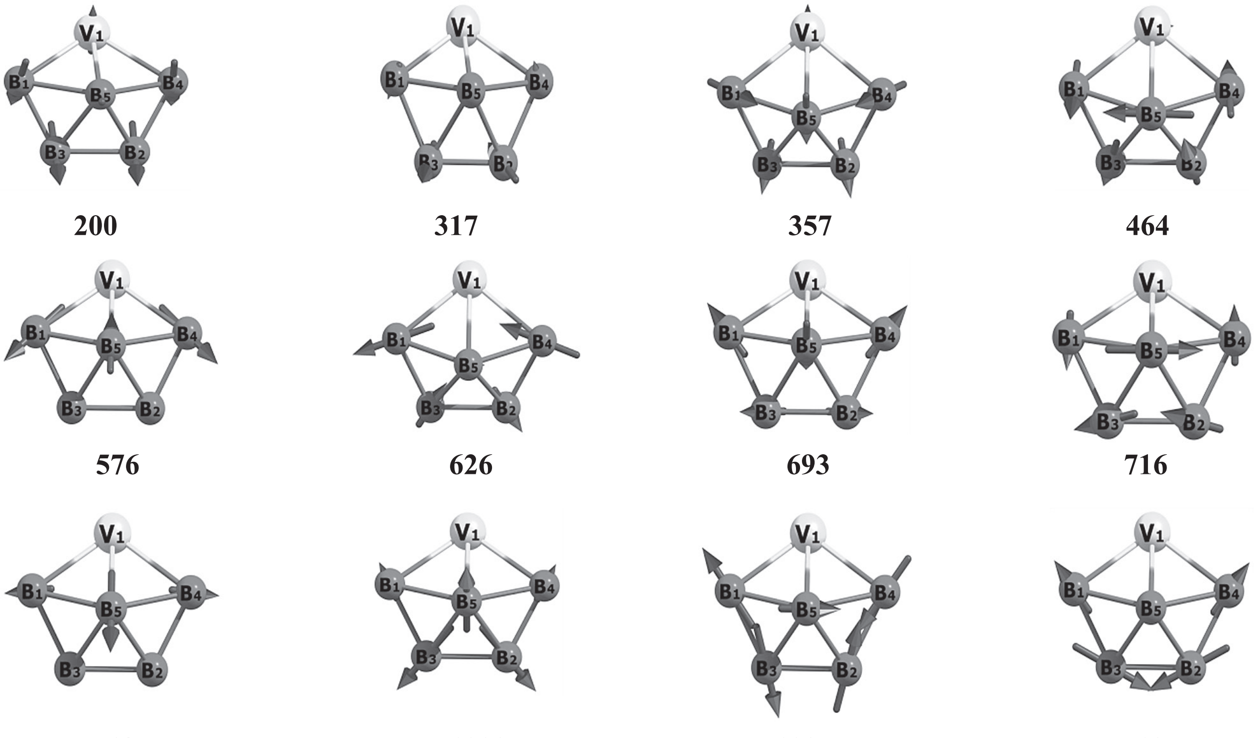
Figure 1. Geometries, spin multiplicities, and relative energies (eV) of the low-lying isomers of VB_5^-cluster as computed at the BPW91/def2-TZVP level

Table 1. The computed spin multiplicities (M), relative energies (RE), and vibrational frequencies of the low-lying isomers of VB_5^- clusters

isomer	M	RE (eV)	frequencies (cm^{-1})
A–VB_5^-	2	0.00	200, 317, 357, 464, 576, 626, 693, 716, 764, 1000, 1027, 1078
A–VB_5^-	4	0.26	227, 288, 387, 429, 494, 619, 627, 792, 796, 997, 1022, 1063
A–VB_5^-	6	0.69	164, 178, 295, 352, 463, 596, 606, 760, 855, 957, 1035, 1062
B–VB_5^-	4	0.42	117, 225, 283, 356, 382, 566, 599, 741, 843, 975, 1082, 1215
B–VB_5^-	6	0.46	114, 265, 282, 363, 371, 569, 636, 702, 763, 933, 1118, 1172
B–VB_5^-	2	0.51	134, 306, 336, 353, 404, 502, 658, 727, 846, 964, 1079, 1197
C–VB_5^-	4	0.50	211, 246, 328, 404, 470, 557, 590, 701, 785, 953, 1092, 1162

D–VB_5^-	4	0.60	130, 221, 326, 372, 375, 466, 514, 537, 785, 982, 1196, 1401
D–VB_5^-	2	0.66	108, 227, 232, 377, 380, 444, 465, 508, 790, 956, 1203, 1367
E–VB_5^-	6	0.63	142, 181, 237, 320, 361, 584, 625, 714, 929, 965, 1093, 1197
E–VB_5^-	4	0.73	105, 189, 216, 363, 379, 594, 604, 724, 843, 951, 1094, 1204
E–VB_5^-	2	0.77	168, 203, 271, 375, 411, 570, 635, 720, 833, 981, 1088, 1217
F–VB_5^-	4	0.76	136, 219, 270, 296, 329, 563, 610, 650, 748, 997, 1155, 1233
F–VB_5^-	6	0.76	152, 211, 272, 286, 326, 546, 586, 650, 741, 1009, 1138, 1226
F–VB_5^-	2	0.93	141, 201, 305, 362, 368, 463, 614, 685, 780, 1015, 1142, 1248
G–VB_5^-	4	0.82	157, 194, 317, 386, 394, 433, 524, 631, 680, 1002, 1113, 1276
G–VB_5^-	2	0.99	126, 183, 312, 368, 409, 442, 499, 631, 721, 987, 1122, 1299

The vibrational frequencies and normal modes of the doublet ground state of A-VB_5^- as computed at the BPW91/def2-TZVP are displayed in Figure 2. Because there are 6 atoms in VB_5^-, this cluster exhibits 12 vibrational modes ($3N-6 = 3\times6-6 = 12$). The figure shows that all the vibrational frequencies of A-VB_5^- are positive and they are in the range from 200 to 1078 cm^{-1}. It means that the optimized structure belongs to minimum on the potential energy surface.



200 **317** **357** **464**

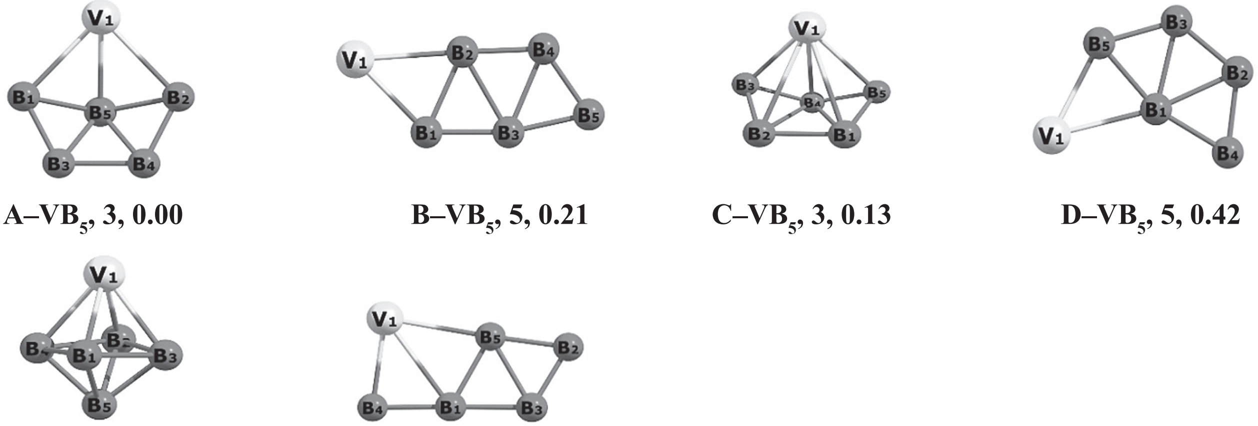
576 **626** **693** **716**

764 **1000** **1027** **1078**

Figure 2. The vibrational frequencies (cm^{-1}) and normal modes of the doublet of A-VB_5^- as computed with the BPW91 and def2-TZVP basis set

3.2. VB_5

The geometry optimization and vibrational frequency calculations for VB_5 were performed on the basis of the optimized geometries of isomers of VB_5^-. The results of the geometry optimization and vibrational frequency calculations for VB_5 cluster are presented in Figure 3 and Table 2. It can be seen that there are 6 important isomers of VB_5. The relative energies of the lowest energy states of these isomers are in the range from 0.00 to 0.89 eV. The most stable isomer is determined to be A-VB_5 with a triplet ground state. The singlet and quintet of the same isomer are above the triplet ground state by 0.08 and 0.46 eV. The quintet of B-VB_5, triplet of C-VB_5, and quintet of D-VB_5 are higher in energy than the ground state by 0.21, 0.13, and 0.42 eV. The other isomers are less stable than the ground state by more than 0.71 eV.



A–VB_5, 3, 0.00 **B–VB_5, 5, 0.21** **C–VB_5, 3, 0.13** **D–VB_5, 5, 0.42**

E–VB_5, 3, 0.71 **F–VB_5, 3, 0.89**

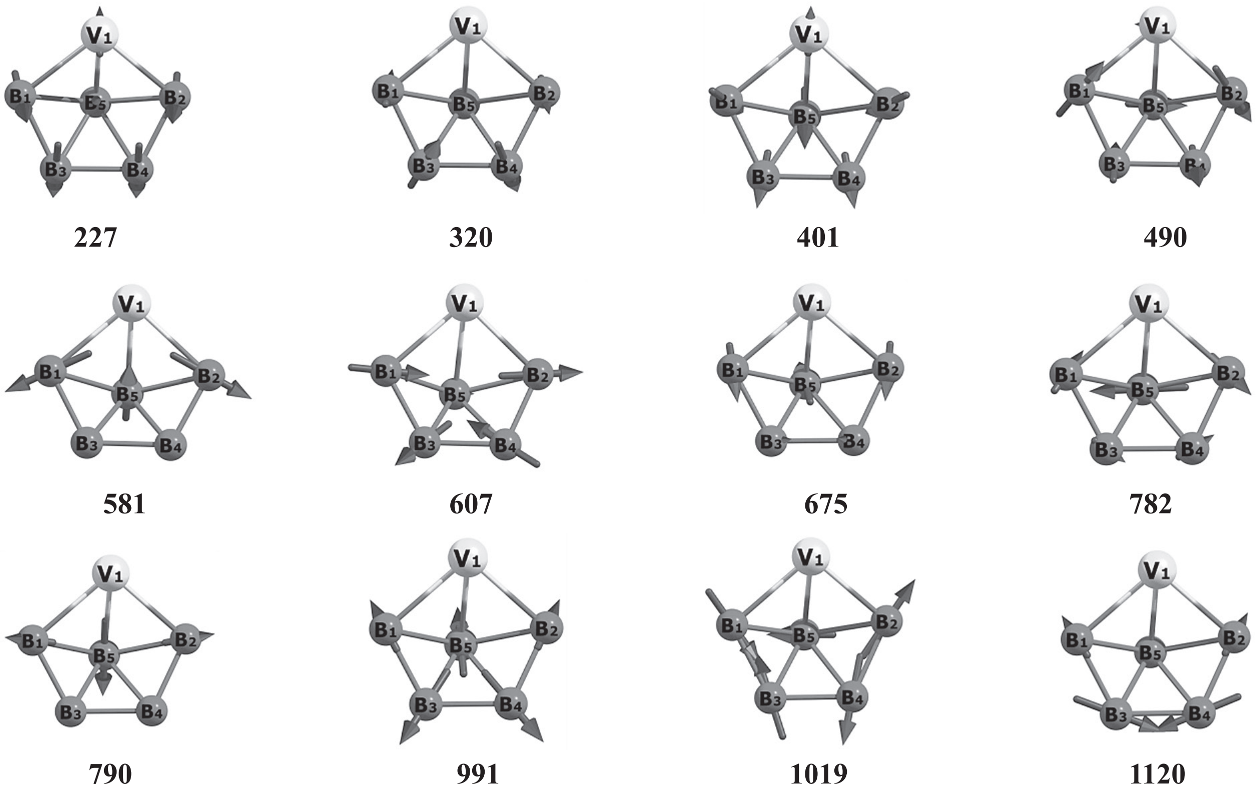
Figure 3. Geometries, spin multiplicities, and relative energies (eV) of the low-lying isomers of VB_5 cluster as computed with the BPW91 functional

Table 2. The computed spin multiplicities (M), vibrational frequencies, and relative energies (RE) of the low-lying isomers of VB_5 clusters

isomer	M	RE (eV)	frequencies (cm^{-1})
A–VB_5	3	0.00	227, 320, 401, 490, 581, 607, 675, 782, 790, 991, 1019, 1120
A–VB_5	1	0.08	232, 310, 412, 480, 584, 609, 686, 750, 793, 965, 1033, 1140
A–VB_5	5	0.46	146, 216, 331, 360, 443, 622, 659, 786, 904, 987, 1061, 1094
B–VB_5	5	0.21	127, 278, 289, 350, 393, 541, 589, 721, 816, 994, 1133, 1223
B–VB_5	3	0.50	127, 200, 300, 323, 396, 488, 636, 712, 806, 1002, 1152, 1199
B–VB_5	1	0.67	153, 318, 329, 357, 423, 497, 612, 736, 817, 983, 1107, 1212
C–VB_5	3	0.13	309, 337, 378, 435, 500, 581, 621, 728, 825, 920, 1102, 1141
C–VB_5	1	0.39	198, 269, 367, 417, 511, 521, 638, 731, 823, 953, 1063, 1112
C–VB_5	5	0.51	143, 298, 342, 416, 478, 516, 600, 739, 900, 927, 1086, 1150
D–VB_5	5	0.42	172, 204, 242, 347, 404, 572, 610, 695, 917, 945, 1067, 1271

D–VB_5	3	0.67	146, 195, 214, 321, 415, 594, 615, 703, 909, 967, 1080, 1265
D–VB_5	1	0.93	215, 227, 268, 376, 421, 594, 630, 713, 856, 967, 1080, 1253
E–VB_5	3	0.71	284, 298, 497, 514, 601, 603, 653, 745, 756, 884, 886, 991
F–VB_5	3	0.89	201, 229, 296, 321, 342, 509, 634, 699, 748, 1076, 1151, 1272
F–VB_5	5	1.07	95, 194, 229, 322, 332, 534, 608, 637, 714, 984, 1104, 1283
F–VB_5	1	1.11	211, 236, 276, 311, 335, 508, 625, 698, 746, 1082, 1150, 1266

The vibrational frequencies of the relevant isomers of the VB_5 cluster are presented in Table 2. It can be seen that all the frequencies are positive. The smallest frequency is around 100 cm^{-1}, while the largest frequency is around 1300 cm^{-1}. The vibrational normal modes of the neutral triplet ground state are displayed in Figure 4. The normal modes with frequencies of 226, 401, 580, 675, 790, 990, and 1119 cm^{-1} are symmetric modes, while the others are antisymmetric modes.



227 320 401 490

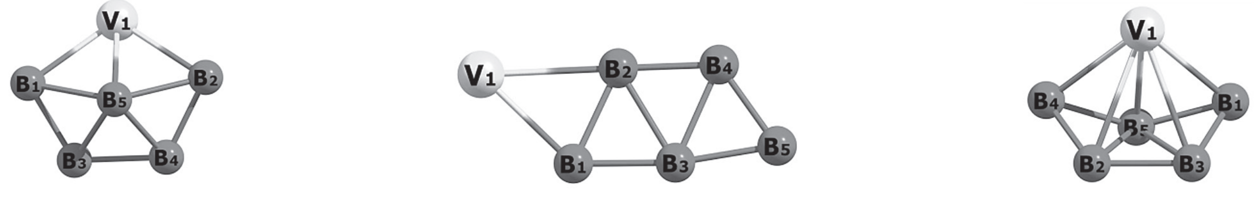
581 607 675 782

790 991 1019 1120

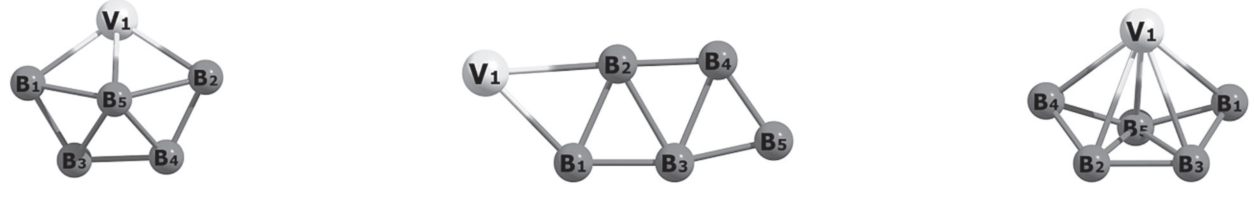
Figure 4. The vibrational frequencies (cm^{-1}) and normal modes of the triplet states of A-VB_5 as computed with the BPW91 and def2-TZVP basis set

3.3. Structures and NPA charges of $VB_5^{-/0/+}$ clusters

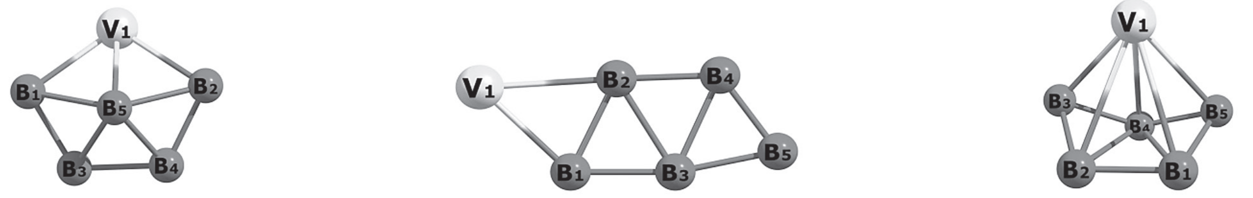
In order to understand the structural variations of the anionic, neutral, and cationic clusters, the important isomers of $VB_5^{-/0/+}$ clusters were collected and presented in Figure 5. It should be noted that the computational results of the anionic and neutral are obtained in this work, while those of the cationic cluster is discussed in the previous work (Tran et al., 2020). It can be seen that the lowest energy states are the doublet, triplet, and doublet of A-$VB_5^{-/0/+}$ isomers. From the anionic to the neutral and cationic cluster, the energy differences among the A, B, and C isomers get smaller and smaller. In particular, the relative energies of the A, B, and C isomers are 0.00, 0.42, and 0.49 eV for the anionic cluster; 0.00, 0.21, and 0.13 eV for the neutral cluster; and 0.00, 0.00, 0.14 eV for the cationic cluster.



A-VB_5^-, 2, 0.00 **B-VB_5^-, 4, 0.42** **C-VB_5^-, 4, 0.50**



A-VB_5, 3, 0.00 **B-VB_5, 5, 0.21** **C-VB_5, 3, 0.13**



A-VB_5^+, 2, 0.00 **B-VB_5^+, 4, 0.00** **C-VB_5^+, 4, 0.14**

Figure 5. The structures, spin multiplicities, and relative energies of the relevant isomers of $VB_5^{-/0/+}$ clusters as calculated with the BPW91 functional

The NPA charges of V1, B1, B2, B3, B4, and B5 atoms of the doublet ground state of A-VB_5^- are estimated to be +0.36, −0.38, −0.38, −0.24, −0.24, and −0.12 e^-. For the neutral ground state, the NPA charges of V1, B1, B2, B3, B4, and B5 atoms of the triplet of A-VB_5 are evaluated to be +0.59, −0.13, −0.13, −0.06, −0.06, and −0.22 e^-. The NPA charges of the doublet of A-VB_5^+ and quartet of B-VB_5^+ were reported in the previous work (Tran et al., 2020). In particular, the NPA charges of V1, B1, B2, B3, B4, and B5 atoms of the doublet of A-VB_5^+ are +0.79, +0.11, +0.11, +0.12, +0.12, and −0.25 e^-, while those of the quartet of B-VB_5^+ are +1.06, +0.00, −0.28, −0.26, +0.06, and +0.42 e^-. It can be seen that from the anionic to the neutral and cationic ground states, the positive charges of V1 atom increases and increases. All boron atoms of the ground states of A-$VB_5^{-/0}$ have negative charges, while some boron atoms of the ground state of A-VB_5^+ and B-VB_5^+ have positive charges. In the case of the quartet of B-VB_5^+, the B5 atom has the largest positive charge (+0.42 e^-). This positive charge is much larger than those of boron atoms of the A-$VB_5^{-/0/+}$. Due to the large positive charge of the B5 atom, the B-VB_5^+ is predicted to have high possibility to activate the C-H bond in CH_4 molecule (Tran et al., 2020).

3.4. Energetic properties of $VB_5^{-/0}$ clusters

Energetic properties of $VB_5^{-/0/+}$ clusters such as adiabatic detachment energy (ADE) and ionization energy (IE) were calculated with the BPW91 functional. Adiabatic detachment energy of the anionic cluster is the energy required to detach one electron of the anion to create the neutral. The adiabatic detachment energy can be calculated via the formula:

$$ADE = E(VB_5) - E(VB_5^-)$$

In this formula, ADE is adiabatic detachment energy, $E(VB_5)$ and $E(VB_5^-)$ are the energies of VB_5 and VB_5^-. Otherwise, ionization energy is the energy needed to eliminate one electron of the neutral to form the cation. Ionization energy is estimated by the formula:

$$IE = E(VB_5^+) - E(VB_5)$$

Table 3. The adiabatic electron detachment energies (ADEs) of the anionic cluster and the ionization energies (IEs) of the neutral cluster as calculated with the BPW91 functional

isomer	transition between spin states	ADE and IE (eV)
$A–VB_5^{-/0}$	2 → 3	1.93
$B–VB_5^{-/0}$	4 → 5	1.73
$C–VB_5^{-/0}$	4 → 3	1.56
$A–VB_5^{0/+}$	3 → 2	7.36
$B–VB_5^{0/+}$	5 → 4	7.15
$C–VB_5^{0/+}$	3 → 4	7.23

The computed results as collected in Table 3 show that the adiabatic detachment energies of the detachment of one electron of the anionic cluster to generate the neutral cluster are 1.93, 1.73, and 1.56 eV for the A, B, and C isomers. The ionization energies of the elimination of one electron of the neutral cluster to form the cationic cluster are calculated to be 7.36, 7.15, and 7.23 eV, respectively. It can be seen that the adiabatic detachment energies of the anionic cluster are much lower than the ionization ones of the neutral cluster. It means that the detachment of one electron of the anionic cluster is much more difficult than the elimination of one electron of the neutral cluster.

4. Conclusion

The relevant geometric structures and vibrational frequencies of a large number of isomers of $VB_5^{-/0}$ clusters are reported based on the BPW91 functional calculations. The $A\text{-}VB_5^{-/0}$ are predicted to be the most stable isomers. These isomers have non-planar pentagonal structure in which the V atom locates at a corner of the pentagon. The ground state of the anionic clusters is doublet and the quartet is 0.10 eV above. The ground state of the neutral cluster is the triplet and the singlet is higher in energy by 0.08 eV. The vibrational frequencies of the $A\text{-}VB_5^{-/0}$ isomers are in the range between 200 cm^{-1} and 1120 cm^{-1}. The B and C isomers are less stable than the A isomer by 0.42 and 0.50 eV for the anionic cluster and by 0.21 and 0.13 eV for the neutral cluster. The other isomers of $VB_5^{-/0}$ clusters are higher in energy than the most stable $A\text{-}VB_5^{-/0}$ by at least 0.42 eV. The NPA charge of V1 atom is positive and it increases from the $A\text{-}VB_5^-$ to $A\text{-}VB_5$ and $A\text{-}VB_5^+$. The B5 atom of the quartet of $B\text{-}VB_5^+$ has the highest positive charge as compared to those of the $A\text{-}VB_5^-$, $A\text{-}VB_5$, and $A\text{-}VB_5^+$. And therefore, the $B\text{-}VB_5^+$ has high reactivity toward methane. The adiabatic detachment energies of the anionic $A–VB_5^-$, $B–VB_5^-$, and $C–VB_5^-$ clusters are calculated to be 1.93, 1.73, and 1.56 eV. The ionization energy of the neutral ground $A–VB_5$, $B–VB_5$, and $C–VB_5$ cluster are estimated to be 7.36, 7.15, and 7.23 eV.

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