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# Geometry and electronic structure of $V_n(\text{Bz})_m$ complexes

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First-principles calculations based on the generalized gradient approximation to the density functional theory are performed to explore the global geometries, ground-state spin multiplicities, relative stabilities, and energetics of neutral and anionic  $V_n(\text{Bz})_m$  ( $n=1-3$ ,  $m=1-4$ , with  $n < m$ ) complexes. The calculated results show that the  $V_n(\text{benzene})_m$  complexes clearly prefer sandwich structures to rice-ball structures. The ground-state spin multiplicities of the  $V_n(\text{benzene})_{n+1}$  complexes increased linearly with the size of the system (i.e.,  $n$ ). In the anionic complexes, the  $V(\text{benzene})_2$  complex is found to be unstable against the autodetachment of the extra electron. The energy difference between adiabatic and vertical electron affinities is found to be very less, indicating negligible ionization-induced structural changes in the ground-state geometries of  $V_n(\text{benzene})_{n+1}$  complexes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1738632]

## I. INTRODUCTION

The interactions of organic molecules with metal atoms and metallic clusters have been studied extensively in the past decade, using both experimental and theoretical methods. Especially the interactions between the transition metal atoms and the benzene molecules have received wide attention recently. In a recent experimental study,<sup>1</sup> the 3d-transition-metal–benzene  $M_n(\text{Bz})_m$  complexes were synthesized in gas phase using the laser vaporization technique. These complexes were analyzed using mass spectroscopy, and their structures are predicted to be either sandwich or rice-ball configurations, depending on the transition metal. Weis *et al.*<sup>2</sup> have performed ion-mobility experiments on cationic  $V_n(\text{Bz})_m$  complexes and proposed multidecker configurations as their likely structures. For the early 3d-transition-metal–benzene complexes, Hoshino *et al.*<sup>3</sup> predicted the geometries to be sandwich structures based on their reaction with  $(\text{CO})_n$  molecules. In another work,<sup>4</sup> Yusuike *et al.* reported the synthesis of  $M_n(\text{Bz})_m$  ( $M=\text{Ti}$ ,  $\text{V}$ , and  $\text{Cr}$ ) complexes and found that these complexes exhibit magic number behavior of  $m=n+1$ . Based on this observation, the authors performed quantum chemical calculations on multidecker sandwich  $M_n(\text{Bz})_m$  complexes. Recently, an IR spectroscopic study<sup>5</sup> was carried out on gas-phase  $V(\text{Bz})^+$  and  $V(\text{Bz})_2^+$  complexes to provide some insights into the structure and spin states of these complexes.

However, in order to get a good quantitative picture of the equilibrium geometries, relative stability, and electronic structure of gas-phase  $M_n(\text{Bz})_m$  complexes, theoretical calculations are necessary, as the above-mentioned experimental studies cannot predict the equilibrium geometries accurately. On the theoretical front, there has been considerable effort towards understanding the geometries of small transition-metal–benzene complexes. Matter and Hamilton<sup>6</sup> have reported density-functional-theory- (DFT-) based results on the ground-state geometries and spin states of neu-

tral and cationic VBz complexes. Bauschlicher *et al.*<sup>7</sup> reported the equilibrium geometries and dissociation energies of cationic transition-metal–benzene complexes using the modified coupled-pair functional method (MCPF) method. Recently, the present authors have reported DFT-based studies<sup>8,9</sup> including gradient corrections through the generalized gradient approximation (GGA) on the geometries and electronic structure of neutral, cation, and anionic  $M(\text{Bz})_m$  ( $M$ =transition metals,  $m=1, 2$ ) complexes. In these calculations, the geometries of  $M(\text{Bz})$  and  $M(\text{Bz})_2$  complexes were restricted only to  $C_{6v}$  and  $D_{6h}$  symmetry, respectively. However, theoretical studies aimed at understanding the equilibrium geometries and electronic structure of large neutral and charged  $M_n(\text{Bz})_m$  complexes are very scarce. The optimized geometries and spectroscopy of neutral and charged  $\text{Ni}_n(\text{Bz})_m$  ( $n \leq 3, m \leq 2$ ) complexes were recently reported by the present authors.<sup>10</sup> In this work, the Ni atoms were found to be caged between the benzene rings, forming what is called rice-ball structures. In the case of  $V_n(\text{Bz})_m$  complexes, however, all the previous theoretical works focused only on either neutral or cationic systems. DFT-based optimized geometries and ionization energies of the multidecker sandwich  $M_n(\text{Bz})_{n+1}$  ( $M=\text{Ti}$ ,  $\text{V}$ , and  $\text{Cr}$ ;  $n=1, 2$ , and 3) complexes were reported recently.<sup>11</sup> Another DFT-GGA-based, ground-state geometry and spin multiplicities of  $V_n(\text{Bz})_m^+$  complexes were reported by Weis *et al.*<sup>2</sup> Hence there are no previous theoretical calculations concentrated on anionic  $V_n(\text{Bz})_m$  complexes.

In this paper, we report the results of a theoretical study of neutral and anionic  $V_n(\text{Bz})_m$  ( $n=1-3$ ,  $m=1-4$ , with  $n < m$ ) complexes. Specifically, we have performed a very extensive search in identifying the global geometries, total energies, and ground-state spin multiplicities of these complexes. We have examined the role of the extra electron on the geometry and spin multiplicities of the complexes. We also report the electron affinities, ionization potentials, and

dissociation energies of  $V_n(\text{Bz})_m$  complexes. Though the neutral  $V_n(\text{Bz})_m$  complexes have been reported earlier,<sup>9–11</sup> the optimization of geometries and spin multiplicities of neutral  $V_n(\text{Bz})_m$  was necessary as it allows us to assess the differences in the structural and electronic properties of the neutral and anion complexes at the same level of theory. It is to be noted here that this is the first systematic theoretical study to report the geometry and ground-state spin multiplicities of anionic  $V_n(\text{Bz})_m$  complexes. Furthermore, to the best of our knowledge, none of the previous studies have reported the dissociation energies and electron affinity values of  $V_2(\text{Bz})_3$  and  $V_3(\text{Bz})_4$  complexes.

The rest of the paper is organized as follows. The computational method employed in this work will be discussed briefly in the next section. In Sec. III, the results for neutral and anionic VBz complexes will be presented and discussed. We first discuss the equilibrium geometries and ground-state spin multiplicities of VBz complexes, followed by a discussion of their electron affinity, dissociation energy, and ionization potentials. Finally, we summarize our results in Sec. IV.

## II. COMPUTATIONAL PROCEDURE

The electronic structure calculations of neutral and negatively charged  $V_n(\text{Bz})_m$  ( $n=1-3$ ,  $m=1-4$ , with  $n < m$ ) complexes were carried out in the framework of DFT, using the GAUSSIAN 98 (Ref. 12) program suite. The GGA to DFT was used in all these calculations. The gradient corrected exchange functional due to Becke,<sup>13</sup> combined with the gradient-corrected Perdew–Wang<sup>14</sup> correlation functional (BPW91) is employed for these calculations. The reliability of the said theoretical method and the basis set was confirmed in our previous calculations of  $Ni_n(\text{Bz})_m$  complexes.<sup>10</sup> One may expect that the inclusion of diffuse functions in the basis set will play an important role in determining the ground-state geometries and the energetics of anionic complexes. In our previous study on the anionic  $Ni_n(\text{Bz})_m$  complexes,<sup>10</sup> the importance of the diffuse functions was examined by comparing the results from Lan12dz and 6-311++G\*\* basis sets. It was found that there is a very small but negligible difference between the results from these two basis sets. Therefore, in the current calculations, we have not considered the inclusion of diffuse functions in the basis sets.

In the geometry optimization procedure, a two-step approach was used. First, the geometrical parameters of neutral and anionic  $V_n(\text{Bz})_m$  complexes were completely optimized for all the possible spin configurations, using the “frozen-core” Lan12dz (Ref. 12) basis set. As the second step, these optimized geometries corresponding to the ground-state spin multiplicity were reoptimized without any symmetry constraints, using the all-electron 6-311G\*\* basis set. In order to make sure that both the Lan12dz- and 6-311G\*\*-based calculations are leading to the same ground-state spin multiplicity, we have optimized the V–benzene complex for all spin multiplicities using both the frozen-core (Lan12dz) and the all-electron (6-311G\*\*) basis sets and compared the corresponding results. For  $V_n(\text{Bz})_m$  ( $n > 1$ ) complexes, the geometries corresponding to only the Lan12dz ground-state

multiplicity are further reoptimized using the 6-311G\*\* basis set.

## III. RESULTS AND DISCUSSION

### A. Geometries

#### 1. VBz complex

The smallest complexes in the current investigation—namely, neutral and negatively charged VBz—are studied in detail using both the Lan12dz and 6-311G\*\* basis sets. Here, two different structures were considered as initial geometries for geometry optimization: (1) a perfect  $C_{6v}$ -symmetric configuration, in which the V atom is above the benzene ring along the central axis of the benzene plane, and (2) a  $C_1$  configuration, in which the V atom is displaced from the central axis of benzene plane. These two different geometries were completely optimized for all spin multiplicities without any symmetry constraints. In the subsequent subsections, we discuss the details of our search for the global minimum of the VBz complex.

*a. Lan12dz calculations.* In neutral VBz complexes, the geometry optimization of the above-mentioned configurations resulted in either  $C_{6v}$ - or  $C_1$ -symmetric structures, depending on the spin multiplicity of the system, instead of the initial geometries. When the  $C_{6v}$  structure was optimized without any symmetry constraints for spin states, the  $C_{6v}$  symmetry stayed unchanged for the doublet and sextet whereas the quartet state ( $2S+1=4$ ) became a  $C_1$  configuration with the vanadium atom displaced from the central axis of benzene plane. In the  $C_1$  starting configuration, the quartet and sextet spin states retained  $C_1$  symmetry upon optimization. However, the doublet state, when optimized, resulted in a perfect  $C_{6v}$  half-sandwich structure. In summary, the doublet spin state always formed a  $C_{6v}$  configuration; the sextet preferred either  $C_1$  or  $C_{6v}$  depending on the starting configuration, and the quartet always preferred the  $C_1$  configuration, independent of the symmetry of the starting geometry. The energy differences among these spin states are very small, with a maximum difference of 0.08 eV (see Fig. 1). The quartet with  $C_1$  symmetry is the lowest in energy, closely followed by the sextet ( $C_1$  configuration) and doublet ( $C_{6v}$  configuration).

The negatively charged VBz system was studied the same way as the neutral complexes—i.e., by optimizing the geometries corresponding to all spin multiplicities for both the  $C_{6v}$  and  $C_1$  configurations. Here the optimized geometry corresponding to the quintet spin state always has  $C_1$  symmetry, independent of the initial starting configuration. On the other hand, for the remaining spin states ( $2S+1=1, 3$ , and 7), the optimized geometry has  $C_{6v}$  symmetry, for both  $C_1$  and  $C_{6v}$  initial configurations. In these anionic complexes, the  $C_1$  configuration with spin multiplicity of 5 is lowest in energy, closely followed by the triplet state ( $C_{6v}$  configuration), which is about 0.07 eV higher in energy. Relative energies of the geometries corresponding to various spin multiplicities are plotted in Fig. 1.

The ground-state geometry of the VBz cluster is given in Fig. 2. This  $C_1$  structure is slightly Jahn–Teller distorted from the  $C_{6v}$  in that the benzene ring is not completely pla-

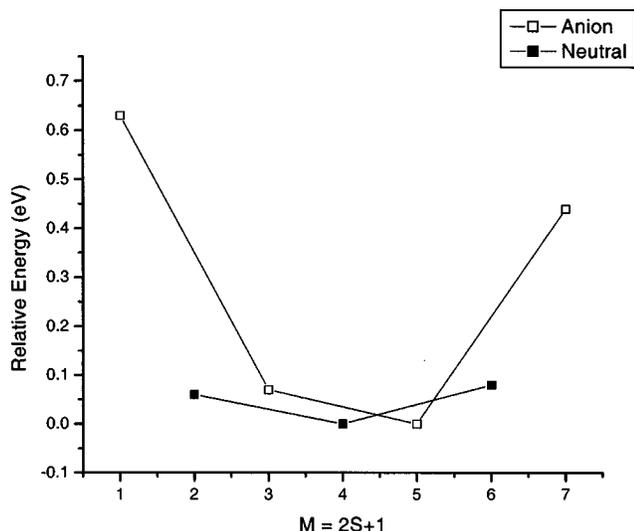


FIG. 1. Relative energies of various spin multiplicities of the VBz complex. The open squares represent the anion complexes, while the solid squares represent the anions. The results are based on BPW91/Lan12dz calculations.

nar. It is very slightly zigzag, which is not noticeable in the figure. The average structural parameters corresponding to this figure are given in Table I.

Clearly, there are some unanswered questions in determining the correct ground-state geometry as well as the correct ground-state spin multiplicity of the VBz complexes. In the previous GGA-DFT-based work<sup>8</sup> (using the DMOL program) by the current authors, the ground-state geometry was found to be a perfect half-sandwich configuration with a spin multiplicity of 6. However, in that study<sup>8</sup> the  $C_1$  configurations were not considered for the geometry optimization. Owing to this ambiguity and the very-low-energy differences among our spin states for the neutral VBz system, we have chosen to repeat the geometry optimization using an all-electron 6-311G\*\* basis set. The results of these calculations and discussion about the correct spin state of the VBz complex are given in the following subsection.

*b. 6-311G\*\* calculations.* The global equilibrium geometry of the neutral VBz complex, calculated using the all-electron 6-311G\*\* basis set, corresponds to a  $C_{6v}$  structure, with the V atom located 1.48 Å above the center of the benzene plane. The C–C and C–H bond distances remain at 1.45 and 1.09 Å, respectively (see Table I). Unlike in Lan12dz-based calculations, here we found the doublet ( $2S$

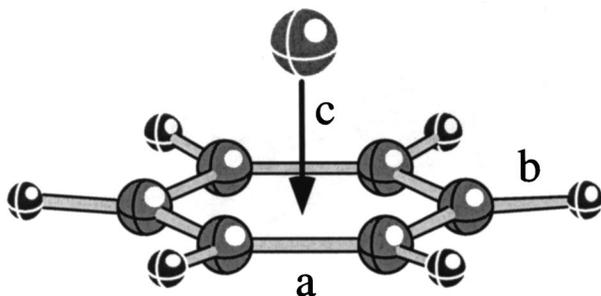


FIG. 2. Ground-state geometry of the VBz complex. The geometrical parameters shown in the figure are given in Table I.

TABLE I. Structural parameters (Å): C–C (A), C–H (B), and V–benzene (C) of ground-state VBz.

	Neutral		Anion	
	Lan12dz	6-311G**	Lan12dz	6-311G**
A	1.58	1.45	1.65	1.44
B	1.09	1.09	1.09	1.09
C	1.45	1.48	1.45	1.53

+1=2) to be the ground-state spin multiplicity. The quartet spin state, which is the ground state in Lan12dz calculations, is now 0.32 eV higher in energy. Figure 3 shows the relative energies of the geometries corresponding to various spin multiplicities. When we compare our neutral VBz ground-state spin multiplicity with those of the earlier works, there are some agreements and disagreements. A previous theoretical work,<sup>6</sup> based on the linear combination of atomic orbitals-local spin density (LCAO-LSD) method, predicted the spin multiplicity as a doublet, which is in agreement with our results. Recent electron paramagnetic resonance (EPR) experiments on matrix-isolated VBz also point to the spin multiplicity as a doublet. However, our calculated spin multiplicity is not in agreement with the results obtained from our previous DMOL-based calculations.<sup>8,9</sup> In that work, using DFT and numerical basis sets, we found the spin multiplicity of 6 to be the ground state. In the present calculation, however, the multiplicity of 6 is 0.89 eV above the doublet state. Weis *et al.*,<sup>2</sup> based on DFT calculations, found the ground-state spin multiplicity of  $\text{VBz}^+$  to be a triplet, followed closely by a quintet ( $\Delta E=2.1$  kcal/mol). The authors, in their paper, hence observe that the ground state of the  $\text{VBz}^+$  system is uncertain and can be either a triplet or quintet. Recent DFT- (B3LYP-) based work by Van Heijnsbergen *et al.*<sup>5</sup> predicted a quintet ground state for the  $\text{VBz}^+$  system. The authors also found the triplet to be next lowest in energy, with an energy difference of only 5 kcal/mol ( $\approx 0.22$  eV).

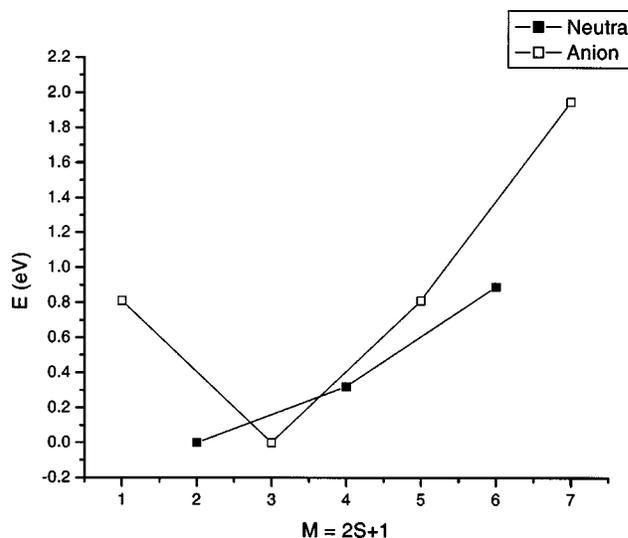


FIG. 3. Relative energies of various spin multiplicities of the VBz complex. Solid squares represent the neutral complex, while open squares represent the anions. The results are based on BPW91/6-311G\*\* calculations.

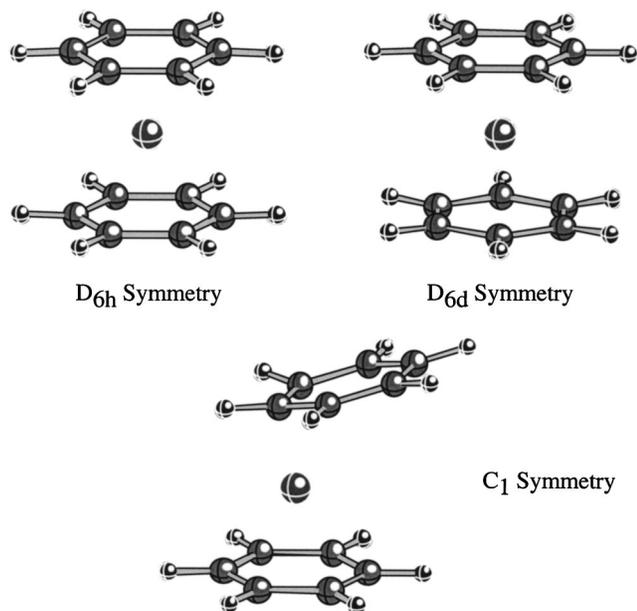


FIG. 4. Three structural configurations of  $V(\text{Bz})_2$ , considered for geometry optimization.

These observations indirectly support our result that the neutral VBz complex can be either a doublet or quartet. In view of the small energy differences between the doublet and quartet spin states, selection of the basis set, and the computational accuracy of our calculations, we conclude the ground state of the VBz complex has a spin multiplicity of 2. Moreover, the ground-state multiplicity of  $\text{VBz}^-$  (a triplet; see below) further supports our conclusion.

For the negatively charged VBz complex, the ground-state geometry is a  $C_{6v}$  configuration in a triplet spin state. The  $C_1$  configuration after optimization became a half-sandwich structure ( $C_{6v}$  symmetry). The benzene-metal distance in the ground state is 1.53 Å, with the C-C and C-H distances in the benzene ring remaining same as that in the neutral VBz complex (see Table I). The quintet spin state, the lowest energy in Lan12dz calculations, is 0.84 eV higher in energy than the triplet spin state. The geometry corresponding to this quintet spin state has  $C_1$  symmetry. The calculated ground-state spin and metal-benzene distance agree with that of our previous DMOL-based DFT-GGA results.<sup>8,9</sup>

As observed from the above discussion, the Lan12dz and 6-311G\*\* calculations may not always lead to the same ground-state spin multiplicity. This contradiction and ambiguity arises when the energy differences between various spin states is too low (e.g., neutral VBz). Hence, during Lan12dz calculations, if we find the energy of any spin state too close to the corresponding ground state ( $\Delta E \leq 0.1$  eV), we considered both of those states for the second step: namely, geometry reoptimization using the 6-311G\*\* basis set. In this way, we can circumvent the ambiguity in the ground-state spin multiplicity.

## 2. $V(\text{Bz})_2$ complex

*a. Lan12dz-based calculations.* In the  $V(\text{Bz})_2$  complex, three different structural configurations were considered for

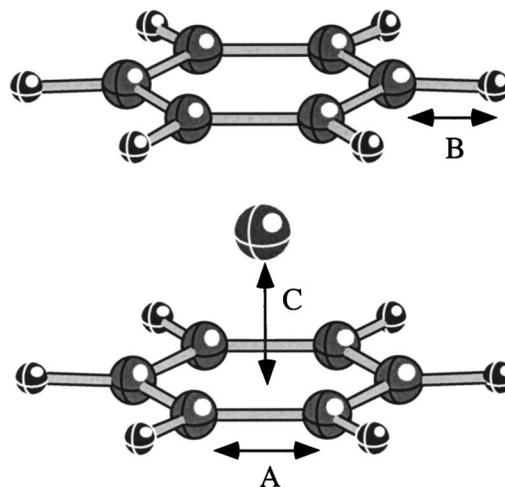


FIG. 5. Ground-state structure of neutral and anionic  $V(\text{Bz})_2$  complexes. The C-C distance, C-H distance, and V-Bz distances are labeled as A, B, and C, respectively, and are given in Table II.

the geometry optimization (see Fig. 4). The first configuration is a normal sandwich structure with  $D_{6h}$  symmetry, in which vanadium atom and benzene rings are arranged alternatively. The second one is a staggered sandwich structure ( $D_{6d}$  symmetry) in which one of the benzene rings is rotated by  $30^\circ$  with respect to the other ring. The third configuration has  $C_1$  symmetry in which the upper benzene ring is tilted with respect to the bottom benzene molecule and the metal atom is below the C-C bond of the upper benzene ring. This configuration is based on the ground-state geometry of  $\text{Ni}(\text{Bz})_2$  obtained from our previous calculations on  $\text{Ni}_n(\text{Bz})_m$  complexes.<sup>10</sup> Geometry optimization was carried out on these three structural configurations for all possible spin multiplicities.

In neutral complexes, the sandwich  $D_{6h}$  structure (Fig. 5) with doublet spin ( $2S+1=2$ ) is lowest in energy in which the vanadium atom is located 1.69 Å from the benzene molecules. This structure is closely followed by the  $D_{6d}$ -symmetric staggered sandwich configuration, again in a doublet spin state with an energy difference of just 0.05 eV. In this staggered sandwich configuration the metal atom is located about 1.70 Å from both the benzene molecules. The equilibrium geometry and the corresponding geometrical parameters of the  $D_{6h}$  configuration are given in Fig. 5 and Table II, respectively. One of the interesting results from these optimization processes is that the  $C_1$  configuration, upon optimization, becomes a perfect sandwich structure with  $D_{6h}$  symmetry. This fact indicates that no matter where we place the V atom and benzene ring they always try to go into

TABLE II. Structural parameters (Å): C-C (A), C-H (B), and V-Bz (C) of ground-state  $V(\text{Bz})_2$  complexes.

	Neutral		Anion	
	Lan12dz	6-311G**	Lan12dz	6-311G**
A	1.44	1.43	1.44	1.43
B	1.09	1.09	1.09	1.09
C	1.69	1.67	1.68	1.66

the symmetric position, forming a sandwich configuration. In summary, the neutral  $V(\text{Bz})_2$  complex has two energetically degenerate ground-state structures, one with  $D_{6h}$  symmetry and the other with  $D_{6d}$  symmetry.

When an electron is added to the  $V(\text{Bz})_2$  complex, the ground-state geometry was found to be again a sandwich structure with  $D_{6h}$  symmetry (Fig. 5). The ground-state spin multiplicity for this anionic system was found to be singlet ( $2S+1=1$ ), with the vanadium being 1.68 Å from the benzene molecules. The  $D_{6d}$ -symmetric structure is again energetically almost degenerate, being 0.06 eV higher in energy than the lowest-energy structure. In this staggered configuration ( $D_{6d}$  symmetry), also the metal ion is 1.68 Å away from the benzene rings. Even in the negatively charged  $V(\text{Bz})_2$  optimization of the  $C_1$  configuration resulted in a perfect  $D_{6h}$  configuration. This proves that unlike  $Ni(\text{Bz})_2$  the  $V(\text{Bz})_2$  complexes (both neutral and charged) prefer perfect sandwich structure.

The anionic  $V(\text{Bz})_2$  complex is found to be unstable against autodetachment of the extra electron (see Sec. III). Judai *et al.*<sup>15</sup> also predicted the anionic  $V(\text{Bz})_2$  to be unstable, which is in good agreement with our calculated results. The triplet spin states of  $D_{6h}$  and  $D_{6d}$  configurations are 0.30 and 0.34 eV higher in energy than the doublet  $D_{6h}$  configuration.

The addition of an extra benzene ring to the neutral  $V(\text{Bz})$  complex did not affect the ground-state spin multiplicity. However, in the anionic  $V(\text{Bz})$  complex the attachment of the second benzene ring has reduced the spin multiplicity from a triplet to a singlet.

*b. 6-311G\*\*-based calculations.* Both the neutral and anionic  $V(\text{Bz})_2$  ground-state geometries obtained from the Lan12dz calculations were further reoptimized using the 6-311G\*\* basis set. Since the  $D_{6h}$ - and  $D_{6d}$ -symmetric sandwich structures were found to be energetically degenerate, both of these geometries in their ground-state spin multiplicity were considered for reoptimization. In these calculations, the preferred spin multiplicity from the earlier calculation (BPW91/Lan12dz) was retained. The reoptimization process was done without any symmetry constraints. After reoptimization of the neutral  $V(\text{Bz})_2$  complex the  $D_{6h}$ -symmetric sandwich configuration was again found to be lower in energy than the  $D_{6d}$  configuration ( $\Delta E = 0.02$  eV). In the negatively charged complex, this energy difference is 0.03 eV.

Since the normal and staggered sandwich structures are energetically nearly degenerate, in order to identify the real ground-state geometry, we have carried out frequency calculations on both of the above sandwich structures. In the case of normal sandwich structure, the calculated vibrational frequencies are all positive, indicating that it is a stable structure. However, the frequency calculation of the staggered sandwich revealed an imaginary frequency in its vibrational spectrum. The imaginary normal mode corresponds to the rotation of the benzene ring about its  $C_6$  axis. Moving the carbon atoms in the direction of the normal mode, corresponding to this imaginary frequency, and reoptimizing the staggered sandwich structure resulted in a stable normal sandwich configuration. It indicates that there is no rotation

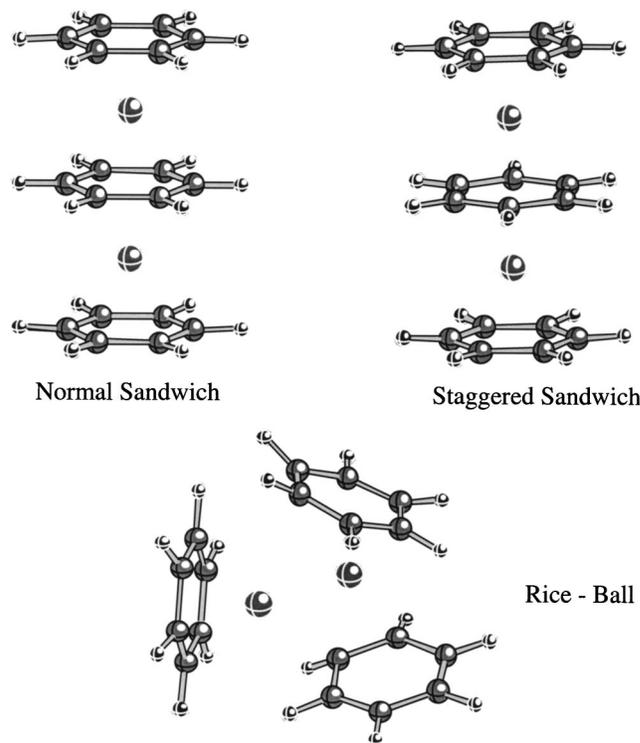


FIG. 6. Three structural configurations of  $V_2(\text{Bz})_3$ , considered for the geometry optimization.

barrier for the benzene rings. Hence the frequency calculation has helped us in identifying the staggered sandwich as a transition state, whereas the normal sandwich with all positive frequencies corresponds to the ground-state geometry.

It is evident from Table II that the geometry of the  $V(\text{Bz})_2$  complex is almost independent of the choice of basis set. Earlier, the current authors, using DFT and numerical basis sets,<sup>9</sup> predicted the benzene–metal distances of neutral and negatively charged  $V(\text{Bz})_2$  complexes to be 1.70 and 1.65 Å, respectively. Another previously reported DFT (B3LYP) study<sup>11</sup> of neutral  $V(\text{Bz})_2$  had considered a sandwich structure for geometry optimization and had reported the various bond distances as V–Bz, 1.675 Å; C–C, 1.426 Å; and C–H, 1.084 Å. Thus our calculated results (both Lan12dz and 6-311G\*\* calculations) are in good agreement with these previously reported results. On comparing the geometrical parameters of neutral and anionic complexes (Table II), it is observed that the addition of an extra electron has induced insignificant changes in the V–benzene distance whereas it has absolutely no influence on the C–C and C–H bond distances. In fact, Judai *et al.*<sup>15</sup> had performed Hartree–Fock-based *ab initio* calculations and had predicted negligible geometric change upon ionization.

### 3. $V_2(\text{Bz})_3$ complex

For  $V_2(\text{Bz})_3$  complexes also, three different structural configurations were considered for geometry optimization (see Fig. 6). Two of these structures are multidecker sandwich structures, with each of the vanadium atoms sandwiched between benzene rings. In one of these structures, the middle benzene ring is rotated by 30° with respect to the two

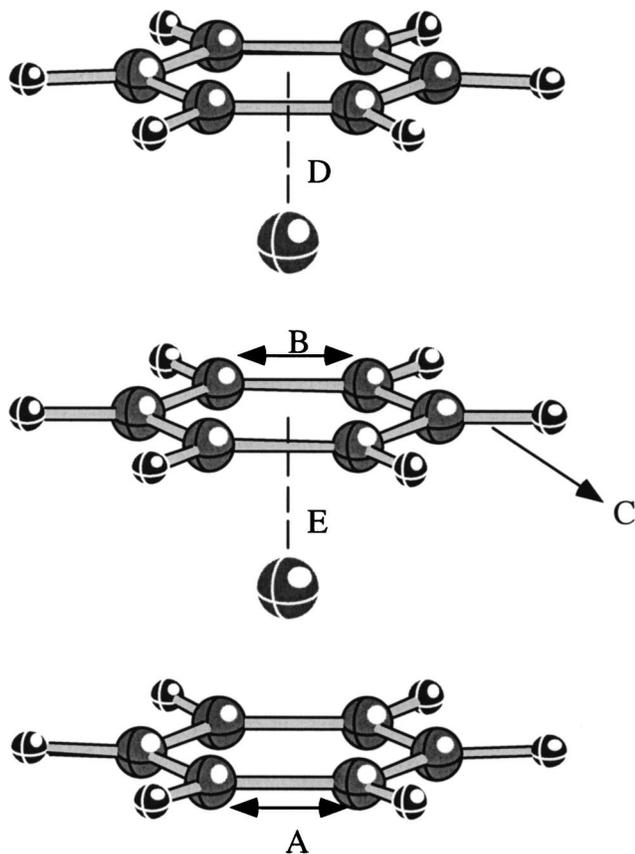


FIG. 7. Ground-state geometry of neutral and anion  $V_2(\text{Bz})_3$  complexes. The geometrical parameters identified in the figure are given in Table III.

terminal benzene rings (the staggered sandwich). The third configuration is called rice-ball structure, in which the two metal atoms are completely covered by the benzene rings, thus allowing the vanadium atoms to form a diatomic cluster. As the first step, geometry optimization, using the Lan12dz basis set, was carried out on all three configurations for different spin multiplicities.

*a. Lan12dz calculations.* In the neutral  $V_2(\text{Bz})_3$  the ground-state geometry is a normal sandwich configuration with the triplet being its spin multiplicity. The staggered sandwich configuration ( $2S+1=3$ ) is energetically degenerate with just 0.09 eV higher in energy than the normal sandwich complex. In the most interesting configuration—namely, the rice-ball structure—the triplet is still lower in energy than the other spin states. However, the rice-ball triplet state is 0.68 eV higher in energy than the triplet normal sandwich configuration. The two sandwich configurations have the same C–C, C–H, and V–benzene distances and the same  $D_{6h}$  symmetry, the only exception being the orientation of the middle benzene ring in the staggered sandwich configuration (which is rotated with respect to the two terminal rings). The geometry and structural parameters of the  $V_2(\text{Bz})_3$  complex are given in Fig. 7 and Table III, respectively. The singlet spin state of the normal sandwich configuration is 0.86 eV (1.20 eV in staggered configuration) higher in energy than the triplet ground state.

In anionic  $V_2(\text{Bz})_3$  complexes, the rice-ball structure and the two multidecker complexes were optimized for spin

TABLE III. Structural parameters (Å): C–C (A) in terminal benzenes, C–C (B) in middle benzene, C–H (C), V–terminal-benzene rings (D), and V–middle-benzene ring (E) of the ground-state  $V_2(\text{Bz})_3$  complexes.

	Neutral		Anion	
	Lan12dz	6-311G**	Lan12dz	6-311G**
A	1.45	1.43	1.45	1.43
B	1.46	1.45	1.47	1.45
C	1.09	1.09	1.09	1.09
D	1.67	1.65	1.68	1.64
E	1.75	1.73	1.71	1.70

multiplicities 2, 4, and 6. For all three structural configurations, the doublet spin state is lower in energy than the remaining quartet and sextet states. However, of all three configurations, the rice-ball structure is again higher in energy ( $\Delta E=0.34$  eV) than both sandwich configurations. The staggered sandwich structure is found to be 0.10 eV higher in energy than the normal sandwich complex. To summarize, the normal sandwich structure is the ground-state geometry of the  $V_2(\text{Bz})_3$  complex, closely followed by the staggered sandwich and rice-ball configuration. Hence, from the  $V(\text{Bz})_2$  and  $V_2(\text{Bz})_3$  calculations, it has been proved conclusively that the vanadium–benzene complexes prefer multidecker sandwich structures to rice-ball configurations.

Upon comparing the geometrical parameters of neutral and anionic complexes in Table III, it is clearly seen that the addition of an electron to the neutral complex did not result in significant changes in the geometrical parameters of either the benzene molecule or vanadium–benzene distances. The only perceptible change is seen in the V–middle-benzene-molecule distance, which decreased by just 0.04 Å (compare entry E in the Table III). These insignificant geometrical changes upon ionization can be due to the accommodation of the extra electron in a nonbonding orbital.

*b. 6-311G\*\* calculations.* As the second step, only the two energetically isomeric multidecker sandwich configurations (normal and staggered) are considered for geometry reoptimization using the all-electron basis set. In the neutral system, similar to that seen in the Lan12dz calculations, both sandwich configurations are energetically degenerate with an energy difference of 0.03 eV. In the case of anions, the energy difference is 0.04 eV. The addition of an extra electron again did not result in any significant changes in the geometry of the system (see Table III).

As we move from the  $V(\text{Bz})_2$  to the  $V_2(\text{Bz})_3$  complex, it is seen that there are no significant changes in the C–C and C–H bond lengths (compare Tables II and III). Hence the addition of a VBz complex to  $V(\text{Bz})_2$  has a very weak influence on the geometrical parameters of benzene molecules. However, unlike in  $V(\text{Bz})_2$ , the vanadium atoms in  $V_2(\text{Bz})_3$  are no longer at equal distances from their neighboring benzene molecules. Upon the addition of the VBz complex to  $V(\text{Bz})_2$ , the vanadium atoms readjust and are closer to the terminal benzenes than the middle benzene molecule (see rows D and E in Table III).

In our previous theoretical study<sup>9</sup> of the neutral  $V_2(\text{Bz})_3$  complex, using the DMOL program suite, the benzene mol-

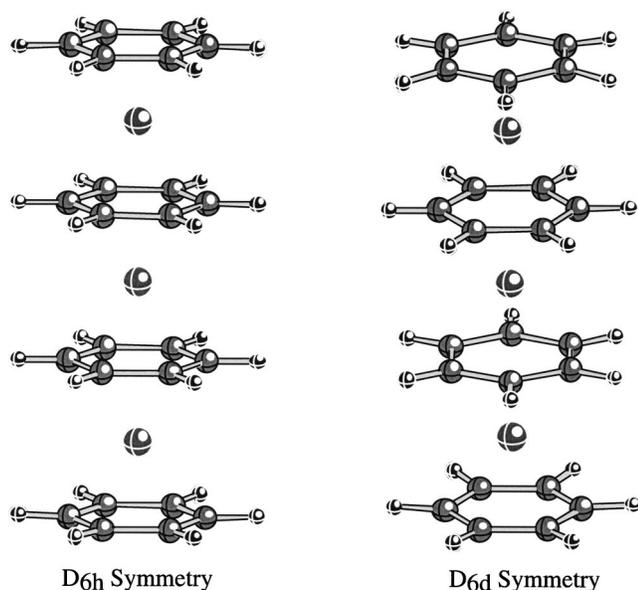


FIG. 8. Two geometrical configurations of the  $V_3(Bz)_4$  complex considered for geometry optimization. The first one is a *normal* sandwich; the second is a *staggered* sandwich.

ecules were frozen, while only allowing the vanadium–benzene distances to vary and the ground-state spin multiplicity of the neutral complex was determined as a singlet. In order to compare the current results on the same footing with that of the reported results,<sup>9</sup> we have performed a similar geometry optimization by freezing the benzene molecules and only allowing the V–Bz distances to vary. The current calculated results, however, show the triplet state to be the ground state, with the singlet being 1.05 eV higher in energy. When we performed a full optimization, without any geometry constraints, the singlet was found to be 0.87 eV higher in energy than the triplet state. Hence we conclude that the ground-state spin multiplicity of  $V_2(Bz)_3$  is indeed a triplet. Moreover, Weis *et al.*,<sup>2</sup> based on a DFT-BLYP-based geometry optimization of  $V_2(Bz)_3^+$ , reported that the ground-state geometry of the cation is a sandwich structure with spin multiplicity of 4. This further supports our current conclusion regarding the ground-state geometry and spin multiplicity of the neutral  $V_2(Bz)_3$  complex. In a DFT- (B3LYP)-based geometry optimization<sup>11</sup> of the neutral  $V_2(Bz)_3$  complex, the authors considered the triplet as the ground-state spin multiplicity and reported the optimized parameters: C–C, 1.48 Å (*middle* Bz), 1.429 Å (*terminal* Bz); V–*terminal*-Bz, 1.648 Å; V–*middle*-Bz, 1.722 Å. Thus our calculated results for neutral  $V_2(Bz)_3$  are in good agreement with this reported work.

The overall affect of the basis set on geometrical parameters of this system is found to be very negligible (see Table III). It is noted that a similar trend was observed in the case of  $V(Bz)_2$  also. Hence, for the largest system under current investigation—i.e., for the  $V_3(Bz)_4$  complex—geometry re-optimization using the all-electron basis set was deemed unnecessary. Moreover, the agreement of our calculated ionization potential (IP) and electron affinity (EA) values with the experimental results (see next section) also has given us the necessary confidence in the accuracy of Lanl2dz basis set

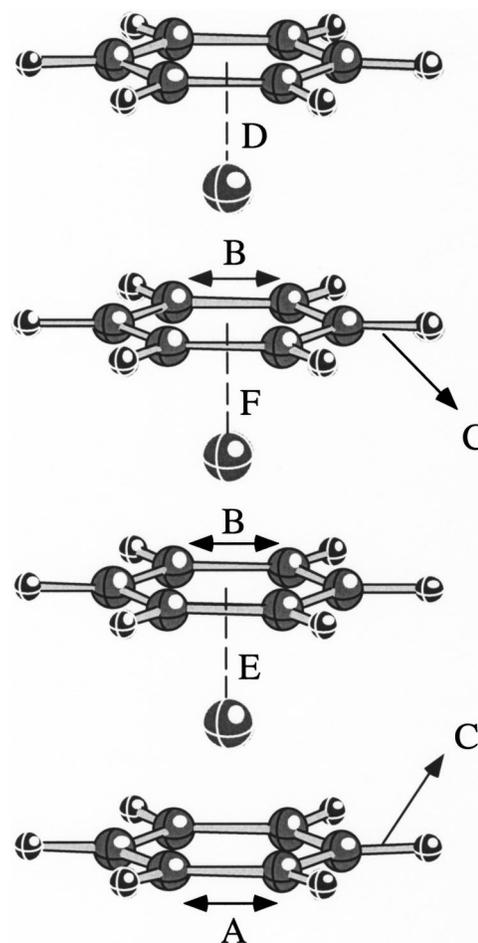


FIG. 9. Ground-state geometry of the  $V_3(Bz)_4$  complex. The geometrical parameters identified in the figure are given in Table IV.

calculations. This step reduced the computational cost significantly without any major compromise in the accuracy of our results.

#### 4. $V_3(Bz)_4$ complex

As mentioned in the above subsection, only Lanl2dz-based calculations were performed for this system. Geometry optimization was performed for two different quadruple-decker sandwich configurations (see Fig. 8): (a) normal sandwich ( $D_{6h}$  symmetry) and (b) staggered sandwich ( $D_{6d}$  symmetry). In the latter case, the benzene molecules are rotated by  $30^\circ$  with respect to their neighboring benzene molecules.

The rice-ball structure can also be a possible candidate for geometry optimization. However, as mentioned in the previous section, it has been proved conclusively that the rice-ball structure is not a preferred configuration of  $V_n(Bz)_m$  complexes. Therefore, based on this observation, rice ball structure is not considered during the geometry optimization of the  $V_3(Bz)_4$  complex.

In neutral complexes, the multidecker configuration with  $D_{6h}$  symmetry in the quartet spin state ( $2S+1=4$ ) is found to be the most stable configuration (Fig. 9), whereas the staggered sandwich multidecker complex is 0.32 eV higher in

TABLE IV. Structural parameters (Å): C–C (A) in *terminal* benzene, C–C (B) in *middle* benzene, C–H (C), V–*terminal*-benzene (D), and V–*middle*-benzene (E), (F) of the ground-state  $V_3\text{Bz}_4$ .

	Neutral	Anion
A	1.45	1.45
B	1.47	1.47
C	1.09	1.09
D	1.66	1.65
E	1.76	1.78
F	1.72	1.68

energy. The geometrical parameters of the neutral and anionic  $V_3(\text{Bz})_4$  complexes are collected in Table IV.

The addition of an electron to the  $V_3(\text{Bz})_4$  complex did not affect the configurational symmetry of the lowest-energy structure, with the staggered sandwich configuration ( $D_{6d}$  symmetry) being unstable by 0.13 eV than the normal sandwich ( $D_{6h}$  symmetry) structure. The ground-state spin multiplicity is found to be a triplet ( $2S+1=3$ ) for both these structural configurations. The  $D_{6h}$  configuration with singlet spin state is 0.67 eV higher in energy.

The geometry relaxation due to the addition of an electron again did not result in any significant changes in the geometrical parameters, with a maximum variation of 2.3% in V–middle-benzene distances. The geometrical parameters of the benzene molecule remained unaffected by the ionization. A similar trend was observed in the smaller  $V_n(\text{Bz})_m$  complexes also. It is also observed that the C–C and C–H bond distances of the benzene molecules remained almost independent of the size and charge of the  $V_n(\text{Bz})_m$  complex. This observation can be exploited in future calculations for larger complexes by freezing the benzene molecules during the geometry optimization processes.

## B. Energetics

In this section, we present and discuss our results for the EA, IP, and dissociation energies ( $D_e$ ) of  $V_n(\text{Bz})_m$  complexes.

The EA is calculated following the definition  $EA = E(\text{neutral}) - E(\text{anion})$ . The adiabatic and vertical electron affinities are compared with the experimental values in Table V. The vertical EA values are computed by detaching the extra electron from the anion, without relaxing the anion geometry, whereas in the adiabatic EA calculations, both the neutral and anionic ground-state geometries were allowed to relax.

TABLE V. Vertical and adiabatic electron affinity (eV) of  $V_n(\text{Bz})_m$  complexes.

	Lan12dz		6-311G**		Expt.
	Vertical	Adiabatic	Vertical	Adiabatic	Adiabatic
VBz	0.52	0.44	0.35	0.30	$0.62 \pm 0.07$
VBz <sub>2</sub>	−0.48	−0.50	−0.38	−0.42	Negative
V <sub>2</sub> Bz <sub>3</sub>	0.16	0.13	0.24	0.21	
V <sub>3</sub> Bz <sub>4</sub>	0.56	0.52			

Our calculated adiabatic EA values (from Lan12dz and 6-311G\*\*) of the VBz complex are in reasonably good agreement with the reported experimental value given by Judai *et al.*,<sup>15</sup> the maximum deviation from the experimental value being 0.32 eV in the case of 6-311G\*\*-based calculations. For the  $V(\text{Bz})_2$  complex, the calculated EA is found to be negative, meaning the anion is unstable against the autodetachment of the extra electron. Judai *et al.*<sup>15</sup> from photoelectron spectra experiments concluded that  $V(\text{Bz})_2$  has a negative electron affinity. An electrochemical study by Elschenbroich *et al.*<sup>16,17</sup> also resulted in a negative EA for  $V(\text{Bz})_2$ . A previous theoretical study, based on Hartree–Fock calculations performed by Judai *et al.* predicted a negative EA value (−1.99 eV) for the  $V(\text{Bz})_2$  complex. Hence our prediction regarding the instability of negatively charged  $V(\text{Bz})_2$  is in good agreement with previous experimental and theoretical works. Experimental values are not available to verify our predicted EA of  $V_2(\text{Bz})_3$  and  $V_3(\text{Bz})_4$  complexes.

We note that the differences between the vertical EA and adiabatic EA of the  $V_n(\text{Bz})_m$  complexes are negligible—with a maximum difference of 0.08 eV (in VBz). This is consistent with the picture discussed in the previous section: namely, the ionization-induced structural changes are not significant in  $V_n(\text{Bz})_m$  complexes. The vanadium atom likes to accommodate an extra electron whereas the benzene dislikes to (has negative EA); hence, it will be interesting to study the response of EA values as we increase the size of  $V_n(\text{Bz})_m$  complexes starting from VBz. We can increase the size of these complexes by adding either (a) a benzene molecule or (b) a V atom or (c) both. The addition of a benzene ring is expected to decrease the EA value significantly, which is clearly seen as we move from VBz to  $V(\text{Bz})_2$ . The addition of a benzene ring to VBz resulted in a negative EA (decreasing the EA by about 0.90 eV in Lan12dz and 0.70 eV in 6-311G\*\* calculations). When we add both benzene and V atoms to a  $V_n(\text{Bz})_m$  complex, two opposite trends compete in influencing the EA value of the resulting system. The addition of the V atom and benzene ring to the  $V(\text{Bz})_2$  complex results in  $V_2(\text{Bz})_3$ , while the EA increases from −0.50 to 0.13 eV. Similarly, as we move further to a bigger system—namely,  $V_3(\text{Bz})_4$ —the EA increases to 0.50 eV (Lan12dz calculations). Hence, when we add both the benzene and V atoms together, the effect of adding the V atom dominates in modifying the EA value of the resulting  $V_n(\text{Bz})_m$  complex.

The stability of neutral  $V_n(\text{Bz})_m$  complexes against dissociation into smaller complexes is studied by calculating the dissociation energies. The calculated dissociation energies of neutral  $V_n(\text{Bz})_m$  complexes along with the available experimental values are compared in Table VI. The dissociation energy of the VBz system is defined as the energy required to dissociate it into individual metal atom and benzene molecules:  $D_e(\text{VBz}) = -[E(\text{VBz}) - E(\text{V}) - E(\text{Bz})]$ . For the remaining  $V_n(\text{Bz})_m$  complexes,  $D_e$  was calculated by the following definitions:

$$D_e[V(\text{Bz})_2] = -[E(\text{VBz}_2) - E(\text{VBz}) - E(\text{Bz})],$$

$$D_e[V_2(\text{Bz})_3] = -[E(\text{V}_2\text{Bz}_3) - E(\text{VBz}_2) - E(\text{VBz})],$$

TABLE VI. Dissociation energies (eV) of neutral  $V_n(\text{Bz})_m$  complexes.

System	$D_e$ (eV)		Expt.
	Lan12dz	6-311G**	
VBz	0.67	2.09	0.79
V(Bz) <sub>2</sub>	3.13	3.64	3.19
V <sub>2</sub> (Bz) <sub>3</sub>	2.32	2.76	
V <sub>3</sub> (Bz) <sub>4</sub>	2.29		

$$D_e[\text{V}_3(\text{Bz})_4] = -[E(\text{V}_3\text{Bz}_4) - E(\text{V}_2\text{Bz}_3) - E(\text{VBz})].$$

The experimental values given in the Table VI are actually empirical values, calculated from the following equations: For the VBz system,

$$D_e[\text{VBz}] = D_e^+[\text{VBz}] + \text{IP}[\text{VBz}] - \text{IP}[\text{V}],$$

and for V(Bz)<sub>2</sub> it is obtained by

$$D_e[\text{V}(\text{Bz})_2] = D_e^+[\text{V}(\text{Bz})_2^+] + \text{IP}[\text{V}(\text{Bz})_2] - \text{IP}[\text{VBz}],$$

where the IPs are experimental values obtained by Kaya and co-workers<sup>3,15</sup> and the  $D_e^+$  are the experimental dissociation energies obtained by Meyer *et al.*<sup>18</sup> The experimental  $D_e$  data for V<sub>2</sub>(Bz)<sub>3</sub> and V<sub>3</sub>(Bz)<sub>4</sub> are not available. However, keeping in view the good agreement between our calculated (Lan12dz) results and the available experimental data, we can conclude that our dissociation energies for V<sub>2</sub>(Bz)<sub>3</sub> and V<sub>3</sub>(Bz)<sub>4</sub> are reasonable values and can be compared to the experimental data, whenever they are available.

The vertical IPs along with the corresponding experimental data are given in Table VII. Note that experimental ionization potential data<sup>3</sup> are available for all  $V_n(\text{Bz})_m$  complexes under the present study. The calculated IP values correspond to the energy difference between the neutral and cationic systems, both at the optimized geometry of the neutral  $V_n(\text{Bz})_m$  complex. Our calculated IP values are in good agreement with the experimental results.<sup>3</sup> The increasing and then a decreasing trend in the IP values can be explained by studying the variations in the highest occupied molecular orbital (HOMO) energy levels with the size of  $V_n(\text{Bz})_m$  complexes. As we go from VBz to V(Bz)<sub>2</sub>, the HOMO level is shifted down to a lower energy, resulting in an increase in IP values. However, when we increase the size of the system to V<sub>2</sub>(Bz)<sub>3</sub> and V<sub>3</sub>(Bz)<sub>4</sub>, it is observed that the HOMO level shifts up to higher energy; hence, IP values are lowered for these systems.

TABLE VII. Vertical ionization potential (eV) of  $V_n(\text{Bz})_m$  complexes.

System	IP (eV)		Expt.
	Lan12dz	6-311G**	
VBz	5.53	5.71	5.11 ± 0.04
V(Bz) <sub>2</sub>	5.87	5.96	5.75 ± 0.03
V <sub>2</sub> (Bz) <sub>3</sub>	4.73	4.82	4.70 ± 0.04
V <sub>3</sub> (Bz) <sub>4</sub>	4.07		4.14 ± 0.05

## IV. CONCLUSIONS

The equilibrium geometries and ground-state spin multiplicities of neutral and negatively charged  $V_n-(\text{benzene})_m$  complexes are calculated here. We have also calculated the electron affinity and vertical ionization energies of  $V_n-(\text{benzene})_m$  complexes. It has been shown that the choice of the basis sets (Lan12dz versus 6-311G\*\*), with the exception of the VBz complex, has no effect on the geometries and energetics of these complexes and the Lan12dz basis set is sufficient for any future calculations of larger complexes. It has been proved conclusively that the ground-state geometries of the  $V_n-(\text{benzene})_{n+1}$  complexes are indeed sandwich structures. All negatively charged  $V_n-(\text{benzene})_m$  complexes, with the exception of the V-(benzene)<sub>2</sub> complex, are found to be stable against auto-detachment of the electron. The electron affinity (vertical and adiabatic) values increased with the size of the system, again the exception being the V-(benzene)<sub>2</sub> complex. The addition of an electron did not affect the ground-state geometries of  $V_n-(\text{benzene})_m$  complexes. It has been observed here that the structural parameters of benzene molecules are not significantly altered by the presence of transition metal atoms. Hence it is claimed here that the benzene molecule can be frozen during the geometry optimization of larger complexes without affecting the accuracy of the results.

## ACKNOWLEDGMENT

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