

## ARTICLE

# Theoretical Study on Geometrical and Electronic Properties of Anionic and Neutral $V_2O_6$ Clusters

Zhao-ying Chen, Jin-long Yang\*

*Hefei National Laboratory for Physical Sciences at Microscale, Laboratory of Bond Selective Chemistry and Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, China*

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The geometrical and electronic properties of the anionic and neutral  $V_2O_6$  clusters were studied with the spin unrestricted hybrid density functional B3LYP method. The calculated ground states of both clusters are different from the previous theoretical results. The ground state of  $V_2O_6^-$  is found to be a doublet with  $C_{2v}$  symmetry, while a doublet with  $D_{2h}$  symmetry was previously obtained by Vyboishchikov and Sauer. For neutral  $V_2O_6$ , the ground state is an open-shell singlet with  $D_{2h}$  symmetry whose energy is very close to that of the triplet state. In contrast, a closed-shell singlet with  $D_{2h}$  symmetry was obtained by Vyboishchikov and Sauer, and Calatayud *et al.* found a triplet ground state with  $C_s$  symmetry. Moreover, the calculated adiabatic and vertical detachment energies of the anion cluster are in much better agreement with the experimental results of photoelectron spectroscopy than previous theoretical values.

**Key words:**  $V_2O_6$ , PES, Spin-unrestricted B3LYP

## I. INTRODUCTION

Vanadium oxides are of special interest due to its ability to catalyze various oxidation reactions [1,2]. Experimental and theoretical studies on divanadium oxide clusters are widely carried out [3-8]. Extensive gas-phase vanadium oxides studies have been performed attempting to provide a molecule-level understanding, of such catalytic processes [9-11].

Previously, Vyboishchikov and Sauer studied the geometrical and electronic properties of the anionic and neutral  $V_2O_x$  ( $x=4-7$ ) using both the hybrid three-parameter exchange-correlation functional (B3LYP) and the Becke's exchange functional in combination with Perdew's correlation functional (BP86) [5]. They gave the ground state of doublet ( $^2B_{1u}$ ) with  $D_{2h}$  symmetry for the anionic  $V_2O_6$  cluster, and the ground state of closed-shell singlet ( $^1A_{1g}$ ) with  $D_{2h}$  symmetry for the neutral  $V_2O_6$  cluster. However, Calatayud *et al.* who studied the cationic and neutral  $V_2O_x$  ( $x=3-7$ ) using the B3LYP functional, gave the triplet ground state with  $C_s$  symmetry for the neutral  $V_2O_6$  [6]. The inconsistency of the group symmetry and spin multiplicity of the ground state of the neutral  $V_2O_6$  cluster is thus necessary to be clarified. Both of Vyboishchikov and Sauer's and Calatayud *et al.*'s calculations employed spin-restricted method for singlet state, thus they did not consider the state of open-shell singlet in their calculations. However, the ground state of open-shell singlet for the  $V_2O_4$  species has been reported recently [4].

For the transition metal dimers with partially occupied d shells, such as  $V_2$  [4],  $Cu_2$ ,  $Fe_2$  [12], and  $Ni_2$  [14] complexes, DFT calculations for the ground states are rather complicated due to the large number of nearly degenerate states and the magnetic coupling between the spins of weakly interacting electrons in d shells at different metal centers. Thus a spin-unrestricted method is needed for both the open-shell and the closed-shell systems. High-spin states can be described within the unrestricted Kohn-Sham scheme using a single determinant, while low-spin states need to be approximated by broken-symmetry approaches [4,12,13].

Recently, Zhai and Wang reported the photoelectron spectroscopy (PES) of  $V_2O_x^-$  ( $x=3-7$ ) [7]. The results showed that the adiabatic detachment energy (ADE) of  $V_2O_6^-$  was overestimated by about 1.20 eV by the B3LYP and about 0.6 eV by the BP86 calculations of Vyboishchikov and Sauer [5]. As the ADE is defined as the total energy difference between the anion and the neutral, even if the neutral is the lowest energy one, the overestimation of the ADE still indicates that the energy of the anionic species is too high, i.e., the  $V_2O_6^-$  species obtained by Vyboishchikov and Sauer [5] should not be the lowest energy one. Additionally, we note that the energy difference between the ADE and vertical detachment energy (VDE) had only about 0.01 eV by Vyboishchikov and Sauer's calculations, which was much smaller than the experimental result ( $\sim 0.34$  eV). All these discrepancies need to be clarified.

In this work, we carry out a reexamination on the anionic and neutral  $V_2O_6$  clusters using the spin unrestricted DFT method. We get the more precise knowledge for their ground states, whose electronic structure and chemical bonding are analyzed in details. A good assignment for all the available features of the experi-

\* Author to whom correspondence should be addressed. E-mail: jlyang@ustc.edu.cn

mental PES spectrum, is also given.

## II. DETAILS OF CALCULATION

The spin-unrestricted Kohn-Sham calculations employ the B3LYP functional [15]. The basis sets employ the triplet- $\zeta$  valence basis sets developed by Schäfer *et al.*, augmented with the polarized p function for vanadium, and with the polarized d function and diffuse s and p functions ( $\zeta=0.0845$  [16]) for oxygen. This B3LYP/TZVP+ method was recently reported to be in good agreement with the complete active-space self-consistent field calculations (CASSCF) for vanadium-oxide species [4].

Harmonic frequencies are calculated to analyze the nature of the stationary points (local minimum or saddle point). Note that the B3LYP may give breaking symmetry solutions to transition metal species with near degenerate valence-bond structures due to the mixing of HF-exchange in the functional, which has been recently pointed out by Zhai *et al.* [7]. For the low-symmetry minima and the high-symmetry saddle points on the shallow potential energy surface of the anionic and neutral  $V_2O_6$  species, we perform single point energy calculations using the unrestricted CCSD(T)/TZVP method [17] and unrestricted Hartree Fock orbitals to check the breaking symmetry problem of the B3LYP functional and find out the real symmetry of the  $V_2O_6$  species.

For the neutral  $V_2O_6$  molecule, the energy of the open-shell singlet ( $E(s)$ ) is estimated from the energy of triplet ( $E(t)$ ) and the broken-symmetry solution ( $E(bs)$ ) by the equation [4,12,13] of  $E(s)=2E(bs)-E(t)$ .

When calculating the VDEs of the  $V_2O_6^-$ , the generalized Koopmans theorem [18] is used, i.e., the VDE for the first electron detachment arising from the HOMO orbital of the anion is calculated by the energy difference of the total energies of the anion and neutral in their ground states at the anion equilibrium geometry, and those from the other occupied orbitals are calculated by adding a energy difference between these orbitals and the HOMO orbital. We employ the standard tight convergence criteria in all the geometry optimizations and the single point energy calculations. All computations are performed with the Gaussian 03 programs [19].

## III. RESULTS AND DISCUSSION

### A. Geometrical structures

All species considered in this work have a planar VOVO ring in the center with two exo-cyclic V–O bonds at both sides. Optimized molecular structures for the anionic and neutral  $V_2O_6$  at the B3LYP level are shown in Fig.1(a-f). The calculations for the minima of anionic and neutral  $V_2O_6$  are rather complicated due to the large number of nearly degenerate valence-bond structures of them. For the  $V_2O_6^-$ , the geometry at the

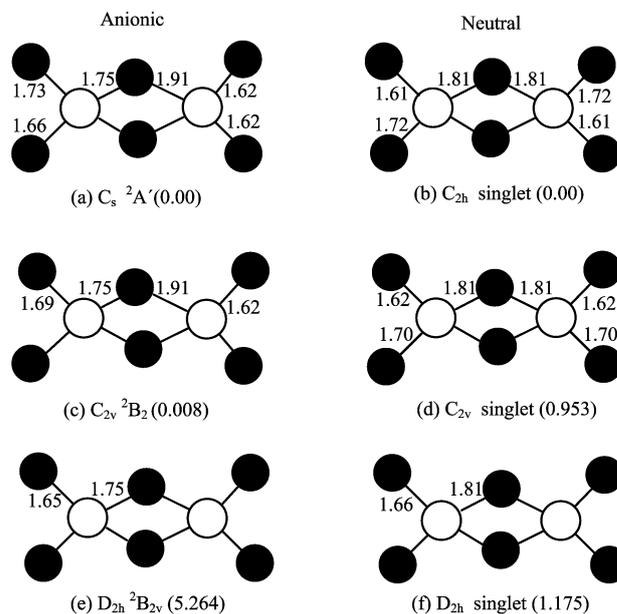


FIG. 1 Optimized molecular structures (bond lengths in Å) and relative energies (unit in kJ/mol) of the anionic and neutral  $V_2O_6$  clusters at the B3LYP level.

B3LYP level converges to a doublet ( $2A'$ ) minima (a) with  $C_s$  symmetry. Whereas the  $C_{2v}$  structure (c) in the doublet  ${}^2B_2$  state is a first-order saddle point with an imaginary frequency of  $-63.65\text{ cm}^{-1}$  ( $B_2$  symmetry). The geometrical differences between these two structures are mainly in the left exo-cyclic V–O bonds: equivalent for the high-symmetric one while nonequivalent for the low-symmetric one. However, their energy difference is only 0.008 kJ/mol, which implies the  $C_s$  minima may be a breaking symmetry solution from the  $C_{2v}$  structure. Actually, the single point energy calculations at CCSD(T) level for these doublet states show that the total energy of the  $C_{2v}$  structure is 29.34 kJ/mol, lower than that of the  $C_s$  structure. The  ${}^2B_{2u}$  electronic state with  $D_{2h}$  structure (e) is also a saddle point at the B3LYP level. It has the same symmetry and bond distances with the ground state of the  $V_2O_6^-$  obtained by Vyboishchikov and Sauer at the B3LYP level [5], although they gave a  ${}^2B_{1u}$  electronic state. Our results show the energy gain due to the  $D_{2h}$ - $C_{2v}$  symmetry reduction has 22.00 kJ/mol. Thus we affirm the ground state of the  $V_2O_6^-$  should be the doublet ( $2B_2$ ) with  $C_{2v}$  structure (c).

For the neutral  $V_2O_6$  species, the geometry at the B3LYP level converges to an open-shell singlet minimum (b) with  $C_{2h}$  symmetry and a less favorable open-shell singlet minimum (d) with  $C_{2v}$  symmetry. Whereas the open-shell singlet with highly-symmetric  $D_{2h}$  structure (f) is a second-order saddle point with the imaginary frequencies of  $-255.32\text{ cm}^{-1}$  ( $B_{1g}$  symmetry) and  $-153.05\text{ cm}^{-1}$  ( $B_{2u}$  symmetry). Their energies are estimated from the corresponding energy of the high-

spin triplet ( $E(t)$ ) and the broken-symmetry solution ( $E(bs)$ ) by the equation [4,12,13] of  $E(s)=2E(bs)-E(t)$ . The results show the energies of the open-shell singlet are only about 0.17 kJ/mol less than those of the triplet state, which indicate the antiferromagnetic coupling between the spins of weakly interacting electrons in d shells at different V centers is quite weak. Note that the maximum energy difference of these open-shell singlet species is only 1.175 kJ/mol, and the geometrical differences of these species are also mainly in the exocyclic V–O bonds. This also suggests that the former two minima may be the breaking symmetry solutions from the highly-symmetric  $D_{2h}$  structure. As expected, the CCSD(T) single point energy calculations for these triplet states show the lowest energy one is the highly-symmetric  $D_{2h}$  structure whose total energy is 0.91 and 1.21 kJ/mol lower than those of the  $C_{2h}$  and  $C_{2v}$  structures respectively. Thus we affirm the ground state of neutral  $V_2O_6$  should be the open-shell singlet with  $D_{2h}$  structure (f), whose energy is very close to the triplet state.

The chemical bonding in the anionic and neutral  $V_2O_6$  species can be understood conveniently using the valence-bond description as shown in Fig.2. The  $C_{2v}$  ground state of the  $V_2O_6^-$  can be understood as a resonance hybrid of two equivalent  $C_s$  structures. With an electron detached from the right  $VO_2$  unit, one of the V=O double bond is destroyed, which lead to the same situation as the left  $VO_2$  unit. The  $D_{2h}$  ground state of neutral  $V_2O_6$  can be understood as a resonance hybrid of two equivalent  $C_{2h}$  or  $C_{2v}$  structures.

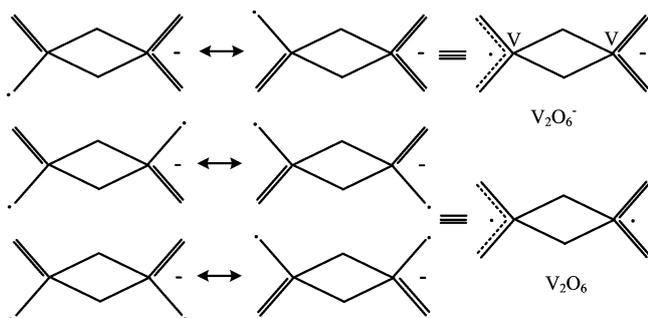


FIG. 2 Valence-bond description of the anionic and neutral  $V_2O_6$  species.

## B. Electronic structures

Figure 3 shows the total spin density of the anionic and neutral  $V_2O_6$  species. For the  ${}^2B_2$  ground state of the  $V_2O_6^-$  (Fig. 3(a)), the extra spin is mainly distributed on the left  $VO_2$  unit, while zero on the right one in which two V=O double bonds are formed. With an electron detached from the anion, the high-spin triplet ( ${}^3B_{3u}$ ) of the neutral  $V_2O_6$  (Fig. 3(b)) has the two excess spins delocalized over both the left and right  $VO_2$  units, which implies the extra electron is detached from

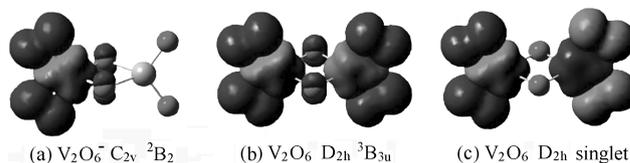


FIG. 3 Spin densities of the anionic and neutral  $V_2O_6$  species. Blue represents the location of maximum spin density.

the right  $VO_2$  unit. Note that both the two V atoms have partially occupied spin electrons (0.38 e. at each V atom by our calculations). The weak antiferromagnetic coupling of the partially occupied  $d_{\pi}$  electrons gives the open-shell singlet ground state as shown in Fig. 3(c).

The Natural Bond Orbital (NBO) population analysis is also performed to get an idea about the electron distributions in the ground states of the anionic and neutral  $V_2O_6$  species. The natural charges are listed in Table I. From which, one can see that the net charges on vanadium atoms differ significantly from the formal oxidation numbers. The charges are delocalized at all the atoms, in spite of the localization of the spin density for the  $V_2O_6^-$  species as described above, which indicate their molecular orbitals are more strongly polarized towards the atoms without spin than to the atoms with spin.

TABLE I The natural atomic charges of the anionic and neutral  $V_2O_6$ . The atoms are labeled by the corresponding cites in Fig.1 (L is the left, M is the middle, R is the right).

	$O_L$	$O_L$	$V_L$	$O_M$	$O_M$	$V_R$	$O_R$	$O_R$
$V_2O_6^-$	-0.43	-0.43	1.19	-0.71	-0.71	1.29	-0.59	-0.59
$V_2O_6$	-0.29	-0.29	1.23	-0.65	-0.65	1.23	-0.29	-0.29

## C. Detachment energies

The calculated ADE and VDEs for the  $V_2O_6^-$  species comparing with experimental results are shown in Table II. The  ${}^2B_2$  ground state of the  $V_2O_6^-$  has the electron configuration of  $[...(12B_2)\uparrow(22A_1)^2(10B_1)^2(3A_2)^2(12B_2)\downarrow(13B_2)\uparrow]$ . The first electron detachment is from the HOMO ( $13B_2$ ) $\uparrow$  orbital of the anion, resulting in a singlet ground state of the neutral species at the anionic equilibrium geometry and giving a VDE of 5.86 eV, which is in good agreement with the experimental value of  $5.95\pm 0.05$  eV. The second electron detachment from the HOMO-1 orbital results in a triplet neutral and gives very close VDE value 5.87 eV to the singlet ground state. And the third electron detachment from the HOMO-2 orbital gives a VDE of 6.45 eV which is also in reasonable agreement with the experimental value ( $6.32\pm 0.02$  eV). The calculated ADE value (5.46 eV) is also close to the experimental value ( $5.61\pm 0.03$ ). Our results show the energy difference between ADE and

TABLE II Calculated detachment energies (in eV) for the  $V_2O_6^-$  compared with experimental PES results (in parentheses).

Detachment channel	Neutral state	ADE		VDE		Assigned state
		This work	Expt.[7]	This work	Expt.[7]	
$(13B_2)^{-1}$	Singlet	5.46	5.61±0.03	5.86	5.95±0.05	X
$(12B_2)^{-1}$	Triplet			5.87		X
$(3A_2)^{-1}$	Triplet			6.45	6.32±0.02	A
$(3A_2)^{-1}$	Singlet			6.71		

VDE, which is related to the relaxation energy from the anionic geometry to the neutral equilibrium geometry, is 0.40 eV, which is close to the experimental result ( $\sim 0.34$  eV). On the contrary, the quite small ( $\sim 0.01$  eV) energy difference between ADE and VDE obtained by Vyboishchikov and Sauer's calculations was due to the fact that they gave almost the same geometry for both the anionic and neutral  $V_2O_6$  species.

#### IV. CONCLUSION

In this paper, we have reported a comprehensive study on the geometrical and electronic properties of the anionic and neutral  $V_2O_6$  clusters using the spin-unrestricted B3LYP method. We find several states near the lowest energy states of the anionic and neutral  $V_2O_6$  species have quite close energies, and the symmetry of the lowest energy state is the lowest, which suggest the breaking symmetry problem of the B3LYP induced by the mixing of HF-exchange in the functional. The single point calculations for these states at the CCSD(T) level verify this. As a result, we get the highly-symmetric ground states for both the anionic and neutral states. For the  $V_2O_6^-$ , the ground state is found to be the doublet with  $C_{2v}$  symmetry. For the neutral  $V_2O_6$ , the ground state is found to be an open-shell singlet with  $D_{2h}$  symmetry, whose energy is very close to the triplet state. The chemical bonding and the NBO for the ground states of both the anionic and neutral  $V_2O_6$  clusters are analyzed in details. A good assignment for all the available features of the PES experiment, is also given.

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