Density Functional Theory Study of Small Vanadium Oxide Clusters†

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Density functional theory is employed to study structure and stability of small neutral vanadium oxide clusters in the gas phase. BPW91/LANL2DZ level of theory is used to obtain structures of VO_y ($y = 1-5$), V_2O_y ($y = 2-7$), V_3O_y ($y = 4-9$), and V_4O_y ($y = 7-12$) clusters. Enthalpies of growth and fragmentation reactions of the lowest energy isomers of vanadium oxide molecules are also obtained to study the stability of neutral vanadium oxide species under oxygen saturated gas-phase conditions. Our results suggest that cyclic and cage-like structures are preferred for the lowest energy isomers of neutral vanadium oxide clusters, and oxygen−oxygen bonds are present for oxygen-rich clusters. Clusters with an odd number of vanadium atoms tend to have low spin ground states, while clusters with even number of vanadium atoms have a variety of spin multiplicities for their ground electronic state. VO_2, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable neutral clusters under the oxygen saturated conditions. These results are in agreement with and complement previous gas-phase experimental studies of neutral vanadium oxide clusters.

1. Introduction

Vanadium oxide based catalysts play an important role in the manufacture of many chemicals.[1] They are, for example, involved in the oxidation of SO_2 to SO_3 in the synthesis of H_2SO_4[2] or selective reduction of NO_x by NH_3.[3] Studying and understanding catalysis in the condensed phase is a very challenging task and therefore many experimental and theoretical studies focus on neutral or ionic vanadium oxide clusters in the gas phase as acceptable models for presumed "active sites" on catalytic surfaces. This general approach to metal and metal oxide mediated catalysis was first suggested by Muetterties.[4]

In order to gain a better understanding of vanadium oxide cluster reactivity and its role in catalysis, one should first understand structure and stability of these molecules. Mass spectroscopy techniques have been applied to study neutral[5−7] and cationic,[8−11] as well as anionic,[12] vanadium oxide clusters in the gas phase. Infrared spectroscopy,[13,14] photoelectron spectroscopy,[15−19] and electron spin resonance spectroscopy[20] have also been used to obtain information about structure, electronic states, and stability of ionic vanadium oxide clusters.

Experimental investigations of gas-phase vanadium oxide clusters are complemented by theoretical investigations. Vyboishchikov and Sauer[21] used density functional theory (DFT) with B3LYP and BP86 functionals and a TZVP basis set to obtain structures of neutral VO_y ($y = 1-4$), V_2O_y ($y = 4, 6, 7$), V_3O_8, V_4O_{10}, and V_4O_{11} clusters and their anions. They have also determined structures of neutral $(V_2O_5)_n$ ($n = 1-5, 8, 10, 12$) clusters at the BP86/DZVP, TZVP levels of DFT.[22] Vyboishchikov also used BP86/DZVP to determine structures and electronic states of $V_2O_y^+$ ($y = 4-6$) cations. Sauer and Döbler[23] further used DFT employing BP86, PBE, and B3LYP functionals with the TZVP basis set to study structure and reactivity of $(V_2O_5)_n$ clusters and model clusters for V_2O_5 supported on silica and the (001) surface of crystalline V_2O_5. B3LYP/TZVP and DZP levels of theory were also applied to study structures and reactivity of $V_2O_y^+$ ($y = 2-6$) and $V_4O_y^+$ ($y = 8-9$) cations.[24] Calatayud et al.[25−27] employed DFT to study neutral and cationic VO_y ($y = 1-4$), V_2O_y ($y = 2-7$), V_3O_y ($y = 6, 7$), and V_4O_{10} clusters at the B3LYP/6-31G* level of theory. Pykavy and van Wüllen applied ab initio calculations at the CASSCF level to study electronic ground states of $V_2O_4^{+/0/-}$ and $VO^{+/0/-}$ species.[28,29] CASSCF and MR-SDCI have been also used to characterize ground states of VO_2 and VO_3 molecules.[20]

Despite the abundance of experimental and theoretical work, the question of which neutral clusters are the most stable in the gas phase is still open.[11] Systematic behavior of vanadium oxide clusters is also not completely understood. In this work, we employ DFT at the BPW91/LANL2DZ level to explore structures and stabilities of small neutral vanadium oxide clusters in the gas phase. Our aim is to gain better understanding of the systematic behavior of vanadium oxide clusters as well as to attempt an explanation of neutral cluster distributions observed in previous experimental studies.[5,6] To accomplish this, a range of oxygen-deficient to oxygen-rich species is considered in our calculations: VO_y ($y = 1-5$), V_2O_y ($y = 2-7$). V_3O_y ($y = 4-9$), and V_4O_y ($y = 7-12$). Many of these structures have been calculated previously; however, our calculations consider a larger variety of spin states in determining cluster ground electronic state. Structures of neutral VO_5, V_3O_y ($y = 4, 5, 9$), and V_4O_y ($y = 7, 12$) clusters are investigated for the first time computationally.

The goal of our work is to investigate a wide range of oxygen-poor to oxygen-rich vanadium oxide clusters consistently at the same level of theory. This allows us to observe general trends within the series with respect to the stability of neutral vanadium oxide clusters in the gas phase (as reported in this work), as well as with respect to their reactions with SO_2.[30,31]

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TABLE 1: Atomization Energies E_a and Structural Parameters of VO, VO_2, and O_2

parameter	experiment	BPW91/LANL2DZ
E_a: VO	6.44 eV ± 0.20 eV[39]	7.33 eV (6.56 eV)
E_a: VO_2	12.20 eV ± 0.19 eV[38]	13.13 eV (12.36 eV)
E_a: O_2	5.12 eV ± 0.002 eV[40]	4.90 eV
VO: V−O	1.589 Å[40]	1.612 Å
VO_2: V−O	1.589 Å[21,41]	1.633 Å
VO_2: O−V−O	110° [21,41]	110.99°
O_2: O−O	1.208 Å[40]	1.288 Å

2. Computational Methods

All calculations reported in this work are performed employing the BPW91 functional[32,33] and the LANL2DZ basis set.[34] LANL2DZ uses the Los Alamos effective core potential with a double-ζ basis set on vanadium atoms and a D95V basis set[35] on oxygen atoms. The Gaussian 98 program[36] is used for V_xO_y clusters ($x = 1, 2, 3$); Gaussian 03[37] is used for calculations on V_4O_y clusters. Cluster geometries are optimized without any restrictions on symmetry, and energy minima are confirmed by vibrational frequency calculations. A variety of spin states and isomers are investigated. Broken symmetry calculations are also performed for V_2O_y ($y = 2, 3, 4, 6, 7$) and V_4O_y ($y = 7, 8, 9$) clusters in order to describe their antiferromagnetic singlet electronic states.

3. Performance of DFT Calculations

Table 1 shows a comparison between the energetic and the structural parameters obtained from experiment and calculated at the BPW91/LANL2DZ level of theory.

Overall, the agreement between experimental and theoretical data is acceptable. The atomization energies of VO and VO_2 are overestimated by about 1 eV. Note that the error in the atomization energy of VO_2 is carried over from the error in the description of VO. Error in the computed atomization energies arises from the difficulties of obtaining the correct electronic ground state of the vanadium atom. BPW91/LANL2DZ level of theory predicts ^{6}D ($3d^44s$) state to be about 1 eV lower in energy than ^{4}F ($3d^34s^2$), while the experimental data corrected to exclude relativistic effects[42] suggest that the ^{4}F is 0.11 eV lower in the energy than ^{6}D. Similar difficulties are not uncommon in the density functional calculations on the first-row transition metals[43] and are also present in the calculations at the BPW91/TZVP or B3LYP/LANL2DZ levels of theory. This fact should not, however, be of concern for calculations on vanadium oxides, since in the presence of oxygens originally unpaired electrons on vanadium atom will participate in bonding or be mainly localized in the 3d orbitals, leaving 4s orbital unoccupied. Atomization energies of VO and VO_2 shown in Table 1 are computed with the ^{4}F state of vanadium atom, and the numbers in parentheses are obtained using the ^{6}D state.

The theoretical value of 5.8 eV for the dissociation energy of VO_2 ($VO_2 \rightarrow VO + O$) compares very well with the experimental value of 5.77 eV,[38] suggesting a very good agreement with the experimental data for bond strengths of vanadium oxide clusters. BPW91/LANL2DZ also tends to overestimate slightly the bond lengths and bond angles, with the largest error of 0.08 Å for O_2. Vibrational frequencies of VO and VO_2 clusters computed at the BPW91/LANL2DZ level of theory also compare favorably with the experimental values,[40,44] with the largest error of 8%.

One could attempt to improve the level of theory (i.e., use an all-electron basis set on vanadium atoms, test a different functional) to obtain correct ground state for the vanadium atom and thereby improve the atomization energies. Unfortunately, because of the lack of experimental data, there are no data to benchmark the performance of theory for larger vanadium oxide clusters. We have chosen to use BPW91 functional since it incorporates the correlation energy that might be important for proper description of bonding in the clusters containing more than one vanadium atom.[45]

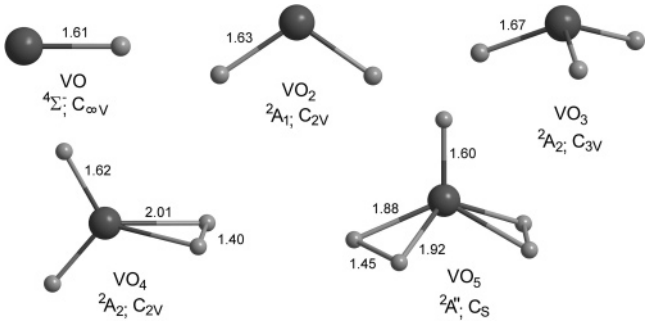

Figure 1. Lowest energy structures of VO_y ($y = 1-5$) clusters.

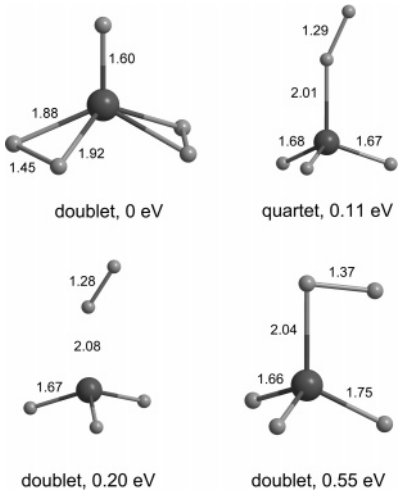

Figure 2. Lowest energy isomers of VO_5.

The overall agreement of the lowest energy structures presented in this work with structures optimized at the B3LYP/6-31G*, BP86/DZVP, and TZVP levels of theory published previously[21,25] suggests that the LANL2DZ basis set is sufficient for our purposes. Geometry for several V_3O_4 clusters is also reoptimized using the BPW91 functional with the LANL2DZ basis set on vanadium and the D95V* basis set on oxygens. No significant differences with BPW91/LANL2DZ level of theory are found. The use of a smaller basis set allows us to perform a large number of calculations to investigate a variety of isomers and spin states, as well as reactions, of the vanadium oxide clusters.

4. Results and Discussion

4.1. VO_x Clusters. Optimized lowest energy structures for VO_y ($y = 1-5$) clusters are shown in Figure 1. Only low lying spin states (doublet through sextet) are considered in the calculations. While the lowest energy structures of VO_2 through VO_5 are doublets, the lowest energy structure of VO is a quartet. This is in accord with previous studies of VO_y clusters.[21] The structure of VO_5 is reported for the first time. VO_5 has several low lying isomers that are shown along with the lowest energy structure in Figure 2. On the basis of our calculations, the VO_5 molecule is a stationary point, though the structures of its low lying isomers suggest that it can easily dissociate into VO_3 and

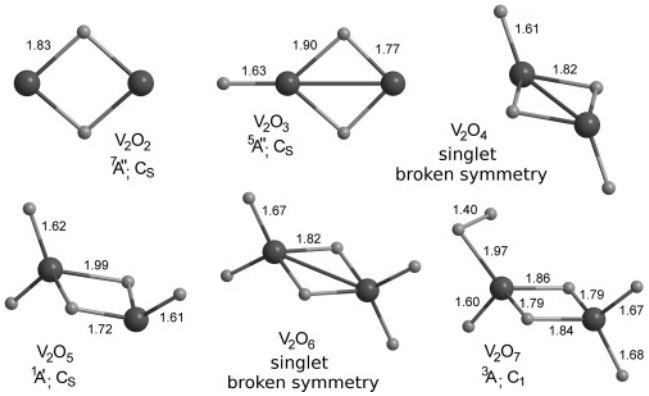

Figure 3. Lowest energy structures of V_2O_y ($y = 2-7$).

O_2 and thus might not be observed experimentally. Structural isomers of VO_3 and VO_4 obtained in our calculations lie at least 0.65 eV above the lowest energy isomers of each cluster.

4.2. V_2O_y Structures. Lowest energy structures obtained for V_2O_y clusters ($y = 2-7$) are shown in Figure 3. Singlet through nonet spin states for the V_2O_2 cluster, singlet through septet states for V_2O_y ($y = 3, 4, 7$) clusters, and singlet, triplet, and quintet states for V_2O_5 and V_2O_6 clusters are considered in the calculations. Spin states of the lowest energy structures vary between singlet and septet depending on the oxygen saturation of a particular cluster. Oxygen deficient clusters tend to have higher spin states, while oxygen-rich clusters prefer lower spin states. The V_2O_4 cluster is an antiferromagnetic singlet in its ground electronic state, with a triplet state lying 0.11 eV above the antiferromagnetic singlet. The ground electronic state of the V_2O_6 cluster is also an antiferromagnetic singlet. The energy difference between the singlet and a triplet state of V_2O_6 is almost negligible (0.004 eV). For V_2O_y ($y = 2, 3, 5$) clusters, preferred spin states can be determined by simple electron counting with unpaired electrons occupying nonbonding d orbitals.

Although structures of the lowest energy isomers are similar to those reported elsewhere,[21,25,29] the spin states determined by our calculations differ in several instances. For example, Calatayud et al.[25] report a triplet as the lowest energy state for both V_2O_2 and V_2O_3, while our results indicate septet and quintet states, respectively. This difference is due to the fact that their set of calculations considered only lower multiplicity states. Vyboishchikov and Sauer[21] report singlet states for neutral V_2O_6 and V_2O_7 clusters. Recently, Chen and Yang[46] performed spin unrestricted B3LYP calculations on V_2O_6 clusters. They concluded that the lowest energy isomer of neutral V_2O_6 is an antiferromagnetic singlet, which is in agreement with our calculations. It is worth noting that antiferromagnetic singlets for V_2O_2, V_2O_3, and V_2O_7 lie relatively close to the ground electronic states of these clusters (0.04−0.18 eV above the ground state).

4.3. $V_2O_y^+$ ($y = 2-7$). To compare structures of neutral V_2O_y clusters and their cations, we have also optimized geometries of $V_2O_y^+$ ($y = 2-7$). The starting geometry for each optimization is the lowest energy isomer of the neutral structure, except in the case of $V_2O_4^+$, for which both cis and trans isomers are considered. Several spin states (doublet through octet for all clusters, and multiplicity 10 in the case of $V_2O_2^+$) are again considered in the calculations. Results are presented in Figure 4.

Optimized structures are in general very similar to the structures of neutral clusters. The lowest energy structure of the $V_2O_4^+$ cluster has a trans conformation as is the case for

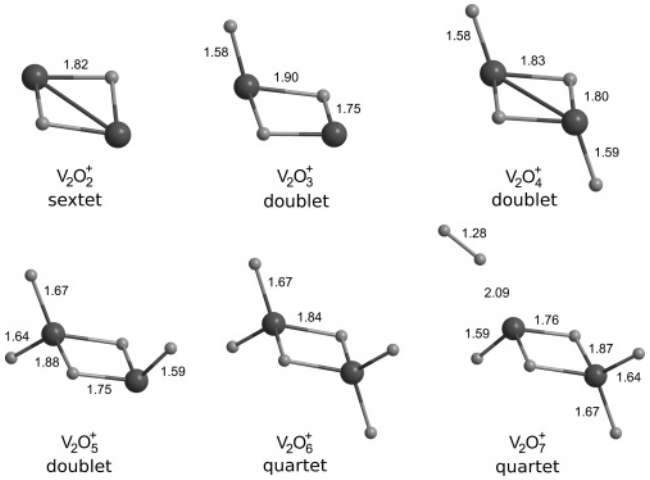

Figure 4. Lowest energy structures of $V_2O_y^+$ ($y = 2-7$).

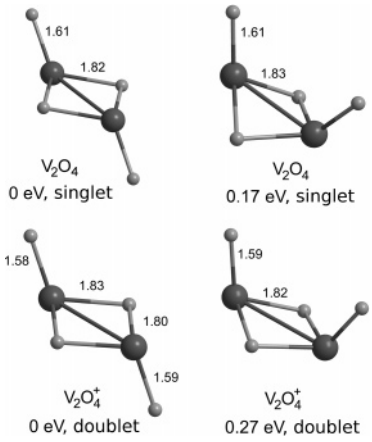

Figure 5. Comparison of V_2O_4 and $V_2O_4^+$ lowest energy structures.

the neutral cluster. Energy differences between cis and trans isomers for both neutral and cation cluster are rather small (see Figure 5). The structure of $V_2O_7^+$ can be viewed as $V_2O_5^+$ with weakly bound O_2, indicating that this cluster can easily lose an O_2 subunit upon ionization.

Structures presented in Figure 4 are not necessarily the lowest energy structures for V_2O_y cations; they are just the lowest energy structures corresponding to the lowest energy neutral isomers of V_2O_y. In other words, these are the isomers we would expect to obtain by ionization of neutral vanadium oxide clusters in a collisionless molecular beam as opposed to the lowest energy isomers of vanadium oxide cations obtained by ablation of vanadium metal into a flow of oxygen. For a more comprehensive study of vanadium oxide cations, see refs 24, 25, and 47.

4.4. V_3O_y ($y = 4-9$). Lowest energy structures of V_3O_y ($y = 4-9$) clusters are shown in Figure 6. We have considered several spin states in the calculations: doublet through multiplicity ten for V_3O_4, doublet through octet for V_3O_5, and doublet through sextet for V_3O_y ($y = 6-9$). All lowest energy isomers are doublets; however, higher spin states for the same general isomeric structures of oxygen deficient clusters (V_3O_4, V_3O_5, and V_3O_6) are energetically very accessible. For example, the energy difference between the sextet and doublet state of the lowest energy isomer of V_3O_4 is only 0.01 eV, and the difference between octet and doublet states for the same isomer is 0.13 eV.

Other reported structures of V_3O_y clusters can be found in the work of Calatayud et al.[25] (V_3O_6 and V_3O_7) and Vyboishchikov and Sauer[21] (V_3O_8).

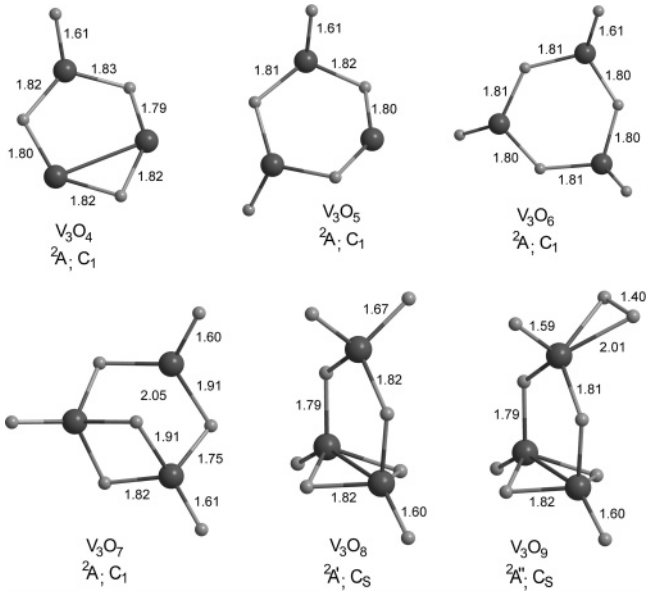

Figure 6. Lowest energy structures of V_3O_y ($y = 4-9$) clusters.

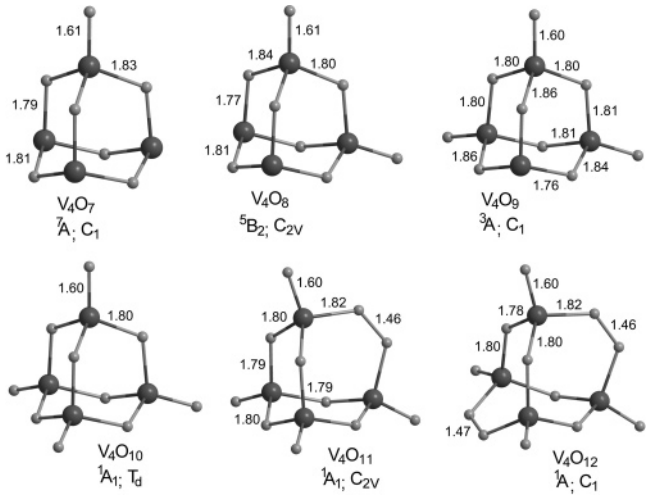

Figure 7. Lowest energy structures of V_4O_y ($y = 7-12$) clusters.

4.5. V_4O_y ($y = 7-12$). Figure 7 shows the lowest energy structures for V_4O_y ($y = 7-12$) clusters. Singlet through nonet spin states are considered for calculations of the V_4O_7 cluster, and singlet through septet spin states are considered for all other V_4O_y ($y = 8-12$) clusters. As in the case of V_2O_y clusters, spin states of the lowest energy structures vary between singlet and septet depending on the oxygen saturation of a particular cluster and can be determined by simple electron counting. Antiferromagnetic singlets of V_4O_y ($y = 7-9$) lie 0.14 to 0.61 eV above the ground electronic states.

Several different isomers of V_4O_y clusters are explored to find the lowest energy structures, except for V_4O_{10}, for which we considered only the cage-like isomer shown in Figure 7. Other isomers of V_4O_{10} are explored in references 21, 22, and 24. In these references, a cage-like structure is found for the lowest energy isomer of V_4O_{10}. Lowest energy isomers of oxygen-deficient V_4O_y ($y = 7-9$) clusters can be all derived from the cage-like structure of V_4O_{10} by removing an appropriate number of terminal oxygens. Additional isomers considered in our calculation (chain-like, cyclic or bridged isomers) are at least 1 eV above the lowest energy cage isomers of V_4O_y ($y = 7-9$), indicating inherent stability of the cage structure.

As for the oxygen-rich V_4O_{11} cluster, the lowest energy isomer determined by our calculations (see Figure 7) differs from that reported by Vyboischikov and Sauer,[21] in which an oxygen−oxygen bond is formed with one of the terminal oxygens. The energy difference between these two isomers is, according to our calculations, 0.27 eV. These structural differences are most likely associated with algorithm differences and are probably within the accepted actual calculational uncertainties for the various DFT approaches. V_4O_{12} also has several low lying isomers (0.14−0.57 eV above the lowest energy one) with oxygen atoms forming oxo-bonds either at the terminal oxygen sites or bridging oxygen sites. These latter oxo-bonds are thus incorporated into the cage structure.

4.5. Stability of Neutral Vanadium Oxide Clusters in the Gas Phase. Previous experimental studies in our laboratory[5,6] address the question of the distribution of neutral vanadium oxide clusters in the gas phase. To understand results obtained in these studies better, we look at the enthalpies (at 298.15 K) of oxidation and reduction reactions of neutral vanadium oxides with oxygen. Under saturated oxygen conditions (i.e., % O_2 in reaction/expansion gas for which the cluster distribution no longer changes, ca. 5%), newly formed vanadium oxides will react with O_2 and grow further, corresponding to the reaction described by $V_xO_{y-1} + O_2 \rightarrow V_xO_y + O$. During the ionization process, vanadium oxide clusters could also fragment by losing an oxygen atom, corresponding to the reaction $V_xO_y \rightarrow V_xO_{y-1} + O$, or by losing an oxygen molecule $V_xO_y \rightarrow V_xO_{y-2} + O_2$. Interplay between these growth and fragmentation reactions for the neutral clusters determines which species will be the most prominent in the gas phase. Enthalpies of the three reactions described here are obtained using the energies of ground state vanadium oxide and oxygen structures (i.e., lowest energy structures) computed at the BPW91/LANL2DZ level of theory and corrected for the zero point energy and thermal effects.

Enthalpies of the reactions are not corrected for basis set superposition error (BSSE), since the BSSE is one order of magnitude smaller than the bonding energies themselves. For example, in case of the $VO_3 \rightarrow VO_2 + O$ reaction, the magnitude of BSSE is 0.11 eV, while the bonding energy of VO_2 with O is 4.34 eV (excluding the ZPE and thermal corrections). Therefore, correcting for BSSE would not change the overall observed trends for the fragmentation and growth reactions of vanadium oxides.

Note that kinetic effects do not need to be considered since increasing the oxygen pressure in the gas-phase experimental studies[5,6] above 5% does not have any further impact on the neutral vanadium oxide cluster distribution. Therefore, thermodynamic stability of the considered clusters is sufficient to explain the experimentally observed results.

The enthalpies of fragmentation and growth reactions for VO_y clusters are shown in Figure 8. The plot shows that the oxidation reactions leading to VO and VO_2 formation are exothermic, while the formation of VO_3, VO_4, and VO_5 by oxidation from clusters with lower oxygen content is not energetically favorable. Oxygen-rich clusters, such as VO_4 and VO_5, loose an oxygen molecule more easily than a single oxygen atom, which can be explained by the presence of oxygen−oxygen bonds in their lowest energy isomers (see Figure 1). Loss of a single oxygen atom is preferable for clusters with lower oxygen content. Overall, our results suggest VO_2 is the most stable cluster under the oxygen saturated conditions, since the formation of VO_2 is exothermic and at the same time it will not be readily oxidized to form VO_3. Additionally, VO_2 will not be easily fragmented into VO or V.

Figures 9−11 show enthalpies of fragmentation and growth reactions for V_2O_y, V_3O_y, and V_4O_y clusters. The trends for these

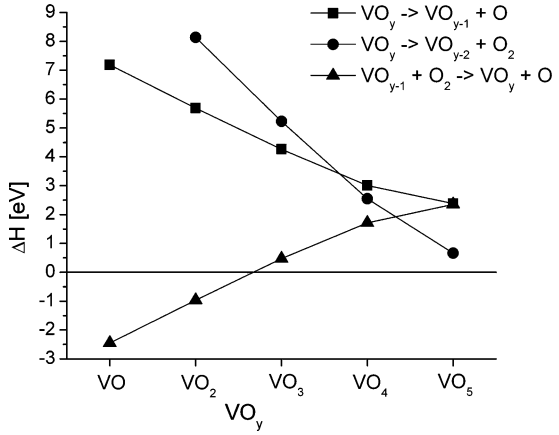

Figure 8. Enthalpies (at 298.15 K) of fragmentation and growth reactions for VO_y clusters.

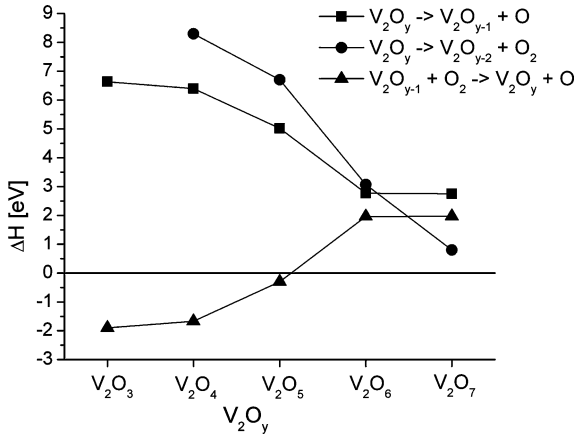

Figure 9. Enthalpies (at 298.15 K) of fragmentation and growth reactions for V_2O_y clusters.

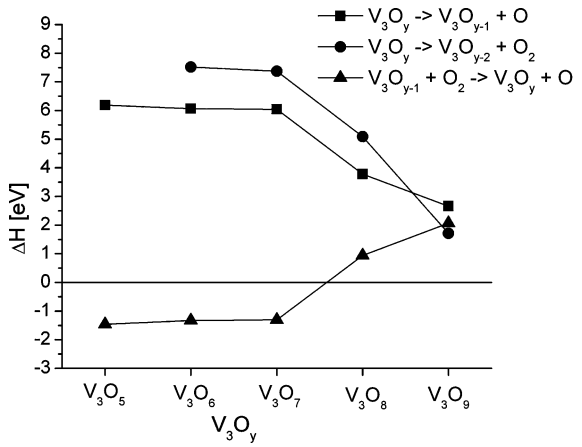

Figure 10. Enthalpies (at 298.15 K) of fragmentation and growth reactions of V_3O_y clusters.

clusters follow the general trend described for VO_y clusters. The vanadium−oxygen bond strength decreases with increasing oxygen content of the clusters, meaning that oxygen-poor clusters are oxidized more easily than the oxygen-rich clusters. Loss of an oxygen molecule is preferred for oxygen-rich clusters, while oxygen-poor clusters are more likely to lose a single oxygen atom. This is again a consequence of oxygen−oxygen bond formation in oxygen-rich clusters. Finally, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable clusters under the oxygen saturated conditions. Formation of these stable

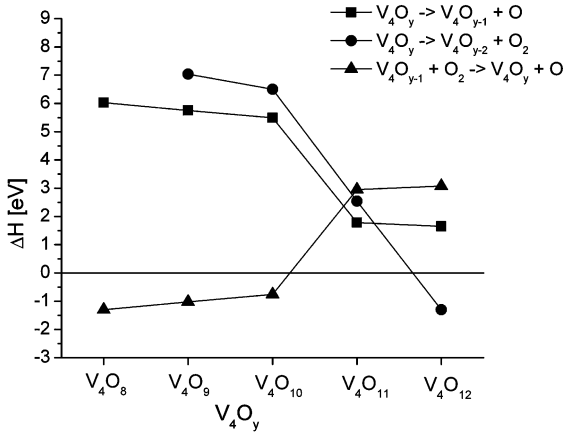

Figure 11. Enthalpies (at 298.15 K) of fragmentation and growth reactions for V_4O_y clusters.

clusters is exothermic; they are not readily oxidized to form clusters with higher oxygen content, and at the same time, they are not easily fragmented by a loss of an oxygen atom or oxygen molecule.

The overall trends obtained from these calculations will hold even if the computational method of our choice did not determine the correct lowest energy isomer or electronic ground state of a particular vanadium oxide cluster. As discussed earlier, the energy differences between some of the lowest energy isomers or spin states can be very small (tenths or hundredths of electronvolts). On the other hand, as seen in Figures 8−11, the overall trends in the enthalpies of fragmentation and growth reactions span across several electronvolts. Therefore, small changes in the energy of a particular vanadium oxide cluster will have virtually no effect on the observed trends.

Previous molecular beam mass spectroscopy studies using 118 nm (10.5 eV) light for neutral cluster ionization[5] show VO_2, V_2O_5, V_3O_7, and V_4O_9 to be dominant in the beam under the oxygen saturated conditions. V_4O_{10} cluster is not observed in this experiment because of its high ionization energy (>10.5 eV). Relative increase in the intensity of V_4O_9 peak under the oxygen deficient conditions is also observed, indicating that a vanadium oxide cluster with higher oxygen saturation than V_4O_9 (for example, V_4O_{10}, as suggested by calculations presented here) is dominant in the molecular beam under the oxygen saturated conditions.

VO_2, V_2O_4, V_3O_7, and V_4O_{10} clusters are found to be the most prominent in the molecular beam under the oxygen saturated conditions detected by single photon ionization studies employing a 26.5 eV X-ray laser.[6] This confirms the stability of V_4O_{10} cluster under the oxygen saturated conditions but raises an additional question of V_2O_4 versus V_2O_5 cluster stability. There are several possible reasons why 10.5 eV ionization and 26.5 eV ionization experiments could yield different results: (1) ionization cross section for V_2O_5 or V_2O_4 can be wavelength dependent and thus yield different intensities in the mass spectra; (2) special resonance can occur between the 26.5 eV and V_2O_4 cluster leading to the relative increase of the $V_2O_4^+$ intensity; and (3) slight variation in the experimental setup in the ablation region can lead to the differences in the synthesis of V_2O_4 and V_2O_5 clusters and thereby influence their relative abundance in the molecular beam as accessed by mass spectroscopy. Which one of these conditions (if any) is responsible for the differences in the experimental data is not clear. It is also worth noting that, except in the case of V_2O_4/V_2O_5 clusters, 10.5 and 26.5 eV ionization studies generate consistent results for many systems, not just V_xO_y clusters.[6]

In addition to studies investigating the stability of neutral vanadium oxide clusters, stability of vanadium oxide cluster cations has also been explored.[11] $V_2O_4^+$, $V_3O_7^+$, and $V_4O_9^+$ species have been determined to be the most stable under the oxygen saturated conditions, suggesting differences in the distribution of neutral and cationic vanadium oxide clusters.

To reiterate, DFT calculations predict VO_2, V_2O_5, V_3O_7, and V_4O_{10} to be the most stable clusters in the size range under oxygen saturated conditions. These results are in agreement with the previous experimental studies of gas-phase distributions of neutral vanadium oxide clusters.

5. Conclusion

In this work, we investigate the structure and stability of small, neutral vanadium oxide clusters in the gas phase. Calculations performed at the BPW91/LANL2DZ level of theory suggest cyclic and cage-like structures for lowest energy isomers of neutral vanadium oxide clusters. Oxygen−oxygen bonds are present for oxygen-rich clusters. Clusters with an odd number of vanadium atoms (VO_y, V_3O_y) tend to have low spin ground states, while clusters with even number of vanadium atoms (V_2O_y, V_4O_y) have a variety of spin multiplicities for their ground electronic state. Ground spin states of oxygen deficient V_2O_y ($y = 2, 3, 5$) and V_4O_y clusters can be determined by simple electron counting. Whether these trends can be generalized to larger clusters, such as V_xO_y ($x = 5-10$; $y = 2x, ..., 3x$), has not been explored.

Enthalpies of growth and fragmentation reactions of neutral vanadium oxide molecules are obtained to study the stability of neutral vanadium oxide species under oxygen saturated gas-phase conditions. Vanadium−oxygen bond strengths in vanadium oxide clusters decrease with increasing cluster oxygen content. Oxygen-rich clusters will lose an O_2 molecule more easily than a single oxygen atom, while the loss of a single oxygen atom is more favorable for oxygen deficient clusters. VO_2, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable neutral clusters under the oxygen saturated conditions. These results are in agreement with and complement previous gas-phase experimental studies of neutral vanadium oxide clusters.

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