

Anion Photoelectron Spectroscopy and Density Functional Study of Small Aluminum–Vanadium Oxide Clusters

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Small aluminum–vanadium oxide clusters, AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2, 3$), were investigated with anion photoelectron spectroscopy and density functional calculations. The adiabatic detachment energies of AlVO_y^- were estimated to be 1.06 ± 0.05 , 1.50 ± 0.08 , and 2.83 ± 0.08 eV for $y = 1, 2$, and 3 . Those of Al_2VO_2^- and Al_3VO_2^- were estimated to be 1.22 ± 0.08 and 1.25 ± 0.08 eV. Comparison of theoretical calculations with experimental measurement suggests that the most probable structure of AlVO^- cluster is quasilinear with O atom in the middle. AlVO_2^- has an irregular chain structure of Al–O–V–O and a C_{2v} cyclic structure very close in energy. The structure of AlVO_3^- cluster is evolved from the C_{2v} cyclic AlVO_2^- structure by adding the third O atom to the V atom. Al_2VO_2^- has a pair of nearly degenerate Al–O–V–O–Al chain structures that can be considered as cis and trans forms. Al_3VO_2^- probably has two low-lying isomers each containing a four-membered ring. The structures of the corresponding neutral clusters are discussed.

1. Introduction

Vanadium oxides are of increasing importance in technological applications, such as industrial catalysis^{1,2} and optical materials.³ Aluminum oxides are widely used in ceramic materials and as catalysts substrates.⁴ Small clusters are considered as good models for understanding the physical and chemical properties of these oxides on a microscopic scale. Thus, extensive experiments have been conducted to study vanadium oxide clusters using mass spectrometry,^{5–9} matrix isolation experiments,¹⁰ electron spin resonance spectroscopy (ESR),¹¹ infrared photodissociation experiments,¹² resonance enhance multiphoton ionization spectroscopy (REMPI),¹³ and anion photoelectron spectroscopy.^{14–17} Aluminum oxide clusters were also studied by mass spectrometry,^{18,19} matrix isolation experiments,^{20,21} infrared predissociation spectroscopy,²² and anion photoelectron spectroscopy.^{23–27} Lots of calculations at various theoretical levels were carried out to investigate the structures and the bonding characteristics of vanadium oxides^{28–36} and aluminum oxides^{37–51} at the ground states and low-lying excited states.

It is also interesting to study the hybrid aluminum–vanadium oxide clusters. In the past few years, it has been found that AlVO_4 shows good sensitivity and selectivity for NO and NO_2 and, thus, may be used as new sensor material.⁵² Raman spectroscopy showed that the V–O–Al interface bond can be regarded as the key active site of oxidation reactions on the vanadia catalyst supported by alumina.⁵³ Very recent studies on the reactions of methane with AlVO_4^+ and Al_3VO_7^+ clusters suggest that hybrid aluminum–vanadium oxide might be useful for gas phase methane activation.³⁶ In this work, we performed an anion photoelectron spectroscopy (PES) study on the small Al_xVO_y^- clusters coupled with density functional theory (DFT) calculations to provide insight into the geometric and electronic properties of aluminum–vanadium oxides.

2. Experimental and Theoretical Methods

2.1. Experimental Section. The experiments were conducted on a home-built apparatus, which have been described in detail elsewhere.⁵⁴ Briefly, the apparatus consists of a laser vaporization source, a time-of-flight (TOF) mass spectrometer, and a magnetic-bottle photoelectron spectrometer. The aluminum–vanadium oxide clusters were generated by laser vaporization of a disk target of Al/V mixture (Al/V mole ratio 8:1). The residual oxygen in the He carrier gas and on the surface of the target was enough for generating Al–V oxide clusters; thus, no additional oxygen was introduced into the source. The formed Al_xVO_y^- cluster anions were mass-analyzed by the TOF mass spectrometer. The mass peaks of Al_xVO_y^- clusters were confirmed by running control experiments with pure Al sample and Al/Ti sample. The cluster anions of interests were mass-selected and decelerated before being photodetached with the laser beam (532 or 266 nm) of a Nd:YAG laser. The kinetic energies of electrons were analyzed by using a magnetic-bottle photoelectron spectrometer. The electron binding energies were obtained according to the equation: $\text{EBE} = h\nu - \text{EKE}$, where EBE is the electron binding energy, $h\nu$ is the photon energy, and EKE is the electron kinetic energy. The photoelectron spectra were calibrated using the known spectrum Cu^- , and the typical energy resolution of the apparatus was ~ 40 meV at electron kinetic energy of ~ 1 eV.

2.2. Theoretical Section. All the calculations reported in this work were performed employing the B3LYP functional^{55,56} implemented in the Gaussian03 program package.⁵⁷ The 6-311+G (2d) basis set was used for Al and O atoms, and the LanL2DZ basis set was employed for the V atom. We tested the theoretical method on AlO and VO. The calculated bond lengths of AlO (1.631 Å) and VO (1.584 Å) are in good agreement with the reported experimental values (1.618 Å for AlO and 1.589 Å for VO).⁵⁸ The electron affinities of AlO and VO from our calculations are 2.54 and 1.02 eV, also close to the experimental data (2.60 eV for AlO²³ and 1.23 eV for VO¹⁴) in the literature. Therefore, the B3LYP method with the mixed basis set

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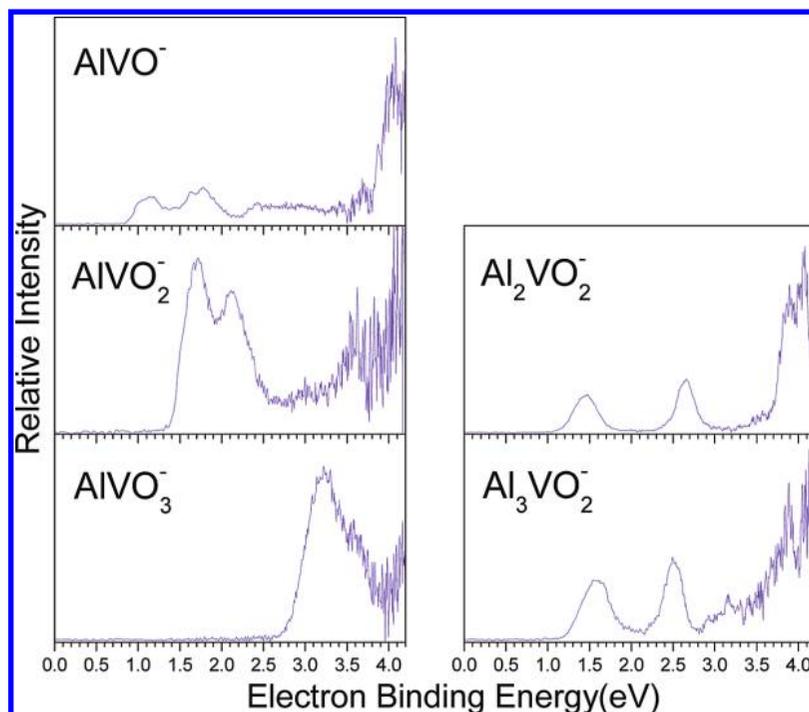


Figure 1. Photoelectron spectra of AIVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2, 3$) cluster anions measured with 266 nm photons.

6-311+G (2d) and LanL2DZ appears to be reasonable to treat the hybrid Al–V oxide clusters. The calculations on the anionic and corresponding neutral clusters were performed at a series of initial structures and spin states. The geometrical structures were optimized without any restriction on symmetry, and the energy minima were confirmed by analyzing the vibrational frequencies. The zero-point energies were included for all calculated energies in this study.

3. Experimental Results

The photoelectron spectra of the AIVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2-3$) clusters taken with 266 nm photons are presented in Figure 1. The low binding energy features of AIVO_{1-2}^- and Al_2VO_2^- were also explored with 532 nm photons, which are shown in Figure 2. Their adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) based on the corresponding photoelectron spectra are listed in Table 1.

In the 266 nm spectrum of the AIVO^- cluster, we can see a broad feature between 0.83 and 1.30 eV followed by two congested peaks centered at 1.63 and 1.78 eV and a broad feature between 2.2 and 3.5 eV. An additional strong feature is observed beyond 3.8 eV. By comparison of the spectra taken with 266 nm and 532 nm photons, it is found that the relative intensities and shapes of the three major features of AIVO^- in these two spectra are different. That can be attributed to the wavelength dependence of photodetachment cross section. As shown in Figure 2, two major features are observed at 1.06 and 1.62 eV. A small feature is observed at 1.46 eV between the two major features. That small feature can be resolved with 532 nm photons in our experiment but is indistinguishable in the 266 nm spectrum due to the low resolution and high noise level at 266 nm. The peak at 1.06 eV corresponds to the transition from $v = 0$ of the ground state of AIVO^- to $v = 0$ of the ground state of AIVO neutral. This implies that the ADE of the AIVO^- is 1.06 eV. The peaks observed at ~ 1.15 and 1.24 eV on the shoulder of the 1.06 eV main feature correspond to the excited vibrations ($v = 1$ and 2, respectively) of the ground state of

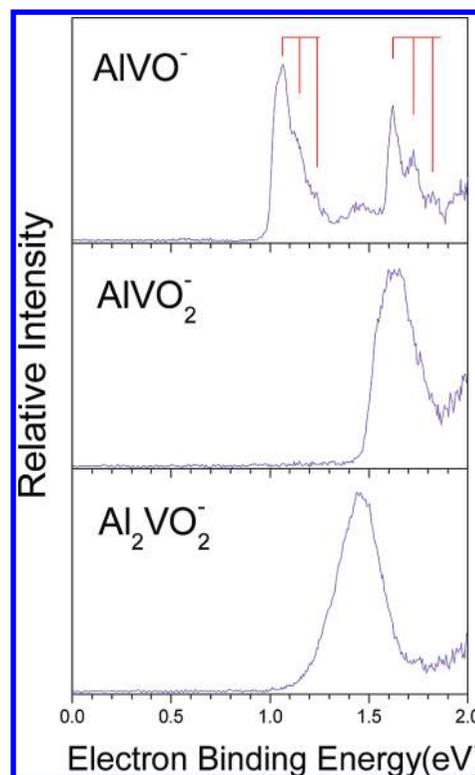


Figure 2. Photoelectron spectra of AIVO_{1-2}^- and Al_2VO_2^- cluster anions measured with 532 nm photons. The vertical lines point to the vibrational structures.

AIVO neutral. We estimated the vibrational frequency of AIVO to be $730 \pm 100 \text{ cm}^{-1}$ based on the spacings of those peaks. According to the relative intensities of the vibrational peaks ($v = 0, 1, \text{ and } 2$), the peak of $v = 0$ has the maximum intensity. Therefore, the peak of $v = 0$ (1.06 eV) also corresponds to the vertical detachment of AIVO^- . Two more weak peaks are also detected at 1.72 and 1.82 eV after the 1.62 eV main feature with spaces of 0.10 eV. Those might come from the vibrational

TABLE 1: VDEs and ADEs of AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2, 3$) Estimated from Their Photoelectron Spectra

cluster	VDE (eV)	ADE (eV)
AlVO^-	1.06(5) ^a	1.06(5) ^a
AlVO_2^-	1.63(8)	1.50(8)
AlVO_3^-	3.22(8)	2.83(8)
Al_2VO_2^-	1.46(8)	1.22(8)
Al_3VO_2^-	1.55(8)	1.25(8)

^a The numbers in parentheses indicate the uncertainties in the last digit.

progression of the excited state of neutral AIVO with a frequency of about $810 \pm 100 \text{ cm}^{-1}$.

In the spectrum of AlVO_2^- taken with 266 nm photons, two main peaks centered at 1.72 and 2.11 eV are observed. Some features might exist on the high binding energy side beyond 2.5 eV but cannot be resolved due to the poor signal-to-noise ratio. The 532 nm spectrum of AlVO_2^- provides better resolution for the first feature with a similar shape, in which the ADE and VDE are determined to 1.50 and 1.63 eV, respectively. The spectrum of AlVO_3^- at 266 nm shows only a broad peak centered at 3.22 eV. The 266 nm spectrum of Al_2VO_2^- shows two major peaks centered at 1.46 and 2.66 eV followed by a strong feature beyond 3.63 eV. The spectrum of Al_2VO_2^- taken with 532 nm photons also shows a similar shape for the first peak with better resolution. As for Al_3VO_2^- , the 266 nm spectrum presents two peaks centered at 1.55 and 2.51 eV and some features higher than 2.8 eV.

4. Theoretical Results and Discussion

To aid in explaining the experimental spectra, we performed density functional calculations on these anionic clusters and their

neutrals. The optimized geometrical structures of the low-lying isomers of AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2-3$) are shown in Figure 3 in the order of increasing energy from left to right. The low-lying structures of neutral $\text{Al}_{1-3}\text{VO}_{1-3}$ clusters are displayed in Figure 4. The calculated relative energies, ADEs, and VDEs of the low-lying isomers are summarized in Table 2 along with the experimental ADEs and VDEs for comparison. The theoretical ADEs were calculated as the energy differences between the anions and the optimized neutrals using the structures of the anions as initial structures.

4.1. AlVO^- . The most stable structure of AlVO^- cluster (1A) in Figure 3 is quasilinear ($\angle\text{AIOV} = 179.9^\circ$) with the O atom in the middle of the Al and V atoms. During the geometrical optimization, it was found that the structure of AlVO^- with $C_{\infty v}$ symmetry was a second-order saddle point in the potential energy surface. That implies that the structure of AlVO^- is not perfectly linear. The structures of isomer 1B and 1C have similar geometrical characteristics with the O atom connecting with the Al and V atoms. Isomers 1B and 1C are 0.36 and 0.77 eV higher in energy than the most stable structure, respectively. Furthermore, their ADEs and VDEs are quite different from the experimental results of AlVO^- as shown in Table 2. The calculated ADE and VDE of isomer 1A, 0.87 and 0.96 eV, are close to the experimental values. So we suggest the isomer 1A is the most probable structure observed under our experimental conditions. Our theoretical calculations show that the most stable structure of AIVO neutral is also quasilinear, similar to the linear structure of Al_2O .^{39,47} The structure of V_2O is reported to be an acute triangle,³⁶ different from the quasilinear structure of AIVO. The calculated antisymmetric stretching frequency of the ground state AIVO neutral is about 890 cm^{-1} after a scale factor of 0.96 recommended for the DFT B3LYP method by Wong.⁵⁹ It is in reasonable agreement with the experimental value ($730 \pm$

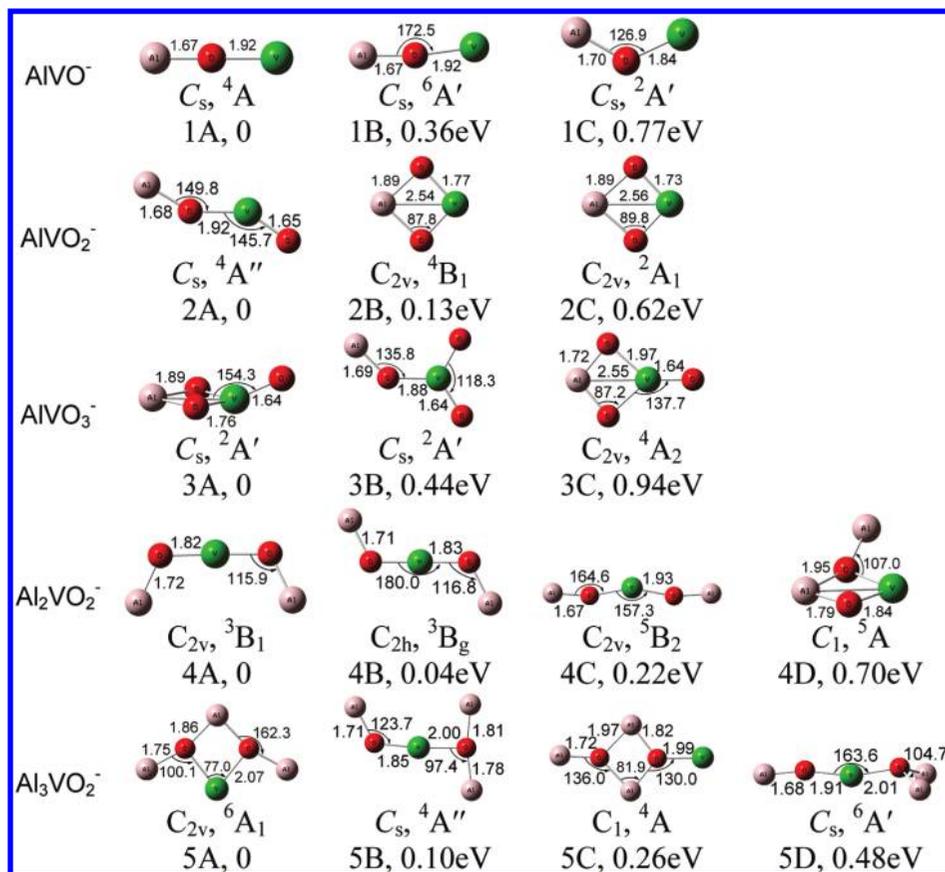


Figure 3. Structures and relative energies of the low-lying isomers of AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2, 3$) clusters. The Al, O, and V atoms are shown in light purple, red, and green, respectively. The bond lengths are in Ångstroms and the bond angles are in degrees.

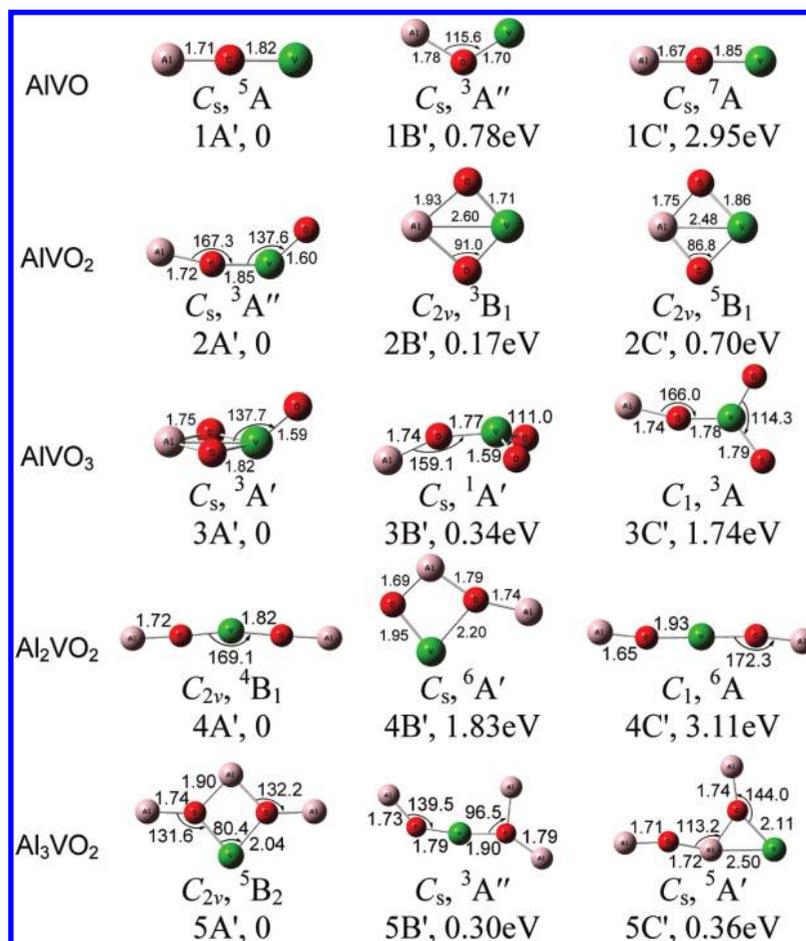


Figure 4. Structures and relative energies of the low-lying isomers of neutral AlVO_y ($y = 1-3$) and Al_xVO_2 ($x = 2, 3$) clusters. The Al, O, and V atoms are shown in light purple, red, and green, respectively. The bond lengths are in Ångströms and the bond angles are in degrees.

TABLE 2: Calculated Relative Energies, ADEs, and VDEs of the Low-Lying Isomers of AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2, 3$) as Well as the Experimental Results for Comparison^a

cluster	symmetry	multiplicity	ΔE (eV)	ADE (eV)		VDE (eV)	
				theor	exptl	theor	exptl
AIVO⁻ (1A)	C_s	4	0	0.87	1.06	0.96	1.06
(1B)	C_s	6	0.36	0.51		0.67	
(1C)	C_s	2	0.77	0.62		0.70	
AlVO₂⁻ (2A)	C_s	4	0	1.57	1.50	1.74	1.63
(2B)	C_{2v}	4	0.13	1.62		1.68	
(2C)	C_{2v}	2	0.62	1.13		1.14	
AlVO₃⁻ (3A)	C_s	2	0	2.85	2.83	3.24	3.22
(3B)	C_s	2	0.44	2.75		3.19	
(3C)	C_{2v}	4	0.94	1.91		2.49	
Al₂VO₂⁻ (4A)	C_{2v}	3	0	0.95	1.22	1.36	1.46
(4B)	C_{2h}	3	0.04	0.91		1.30	
(4C)	C_{2v}	5	0.22	0.73		1.04	
(4D)	C_1	5	0.70	0.25		1.51	
Al₃VO₂⁻ (5A)	C_{2v}	6	0	1.11	1.25	1.40	1.55
(5B)	C_s	4	0.10	1.04		1.22	
(5C)	C_1	4	0.26	1.21		1.51	
(5D)	C_s	6	0.48	0.65		1.13	

^a The most probable structures are denoted in bold.

100 cm^{-1}) obtained in Figure 2. As seen in Figures 3 and 4, the V–O bond in AIVO neutral is shorter than that in AIVO^- anion while the Al–O bond in AIVO neutral is longer than that in AIVO^- anion. That can explain why the antisymmetric stretching mode is active in the photoelectron spectrum.

4.2. AlVO_2^- . The most stable structure of AlVO_2^- , 2A, is an irregular chain arranged in the order of Al–O–V–O with C_s symmetry, while the less stable isomer 2B is a C_{2v} four-

membered ring containing two bridging oxygen atoms. The structure of isomer 2C is similar to that of isomer 2B except the difference of multiplicities. As shown in Table 2, the ADEs and VDEs of 2A and 2B are in agreement with the experimental data. Isomer 2C is 0.62 eV higher than isomer 2A in energy, and its ADE and VDE are much smaller than the experimental values. Therefore, the existence of isomer 2C under the experimental conditions can be ruled out. On the basis of the

above analysis, we tentatively assign isomers 2A and 2B to be the most probable structures in our experiments. It might be possible that one or both of isomers 2A and 2B are present in the experiments. Our calculation found that the lowest-energy isomer of AlVO_2 neutral is also a C_3 bent chain structure in the order of Al–O–V–O similar to the anion. The less stable isomers of AlVO_2 are C_{2v} four-membered rings with two bridging oxygen atoms. The ground state structure of AlVO_2 is different from the ground state structures of Al_2O_2 ^{39,47,50} and V_2O_2 ^{29,35,36}

4.3. AlVO_3^- . The most stable structure of AlVO_3^- (3A) can be considered to be evolved from isomer 2B with the third O atom bonding to the V atom. The third oxygen is out of the plane of the AlVO_2 ring. The ADE and VDE of isomer 3A fit well with the experimental values. The ADE and VDE of isomer 3B are also close to the experimental values; however, isomer 3B is less stable in energy by 0.44 eV. Isomer 3C is higher than 3A by 0.94 eV in energy, and its ADE and VDE are much lower than the experiment measurements. Thus, the existence of isomer 3C in the experiment can be ruled out. Isomer 3A is the most probable structure observed in our experiment. The most stable structure of AlVO_3 neutral is similar to that of AlVO_3^- . The ground-state structures of Al_2O_3 ^{24,47} and V_2O_3 ^{29,36} reported in the literature are also similar to the ground state structure of AlVO_3 .

4.4. Al_2VO_2^- . Isomers 4A and 4B of Al_2VO_2^- cluster are nearly degenerate in energy with isomer 4B higher than isomer 4A by only 0.04 eV. They are all bent chain structures arranged in the order of Al–O–V–O–Al . Furthermore, the Al–O and V–O bond lengths as well as the $\angle\text{AIOV}$ and $\angle\text{OVO}$ angles in these two isomers are almost same. The difference between them is in the bend directions, so the isomers 4A and 4B are considered as a pair of cis and trans structures. The theoretical ADEs and VDEs of isomers 4A and 4B are in reasonable agreement with the experimental data. Hence, we suggest that isomer 4A and 4B coexist in the experiments. The theoretical VDE of isomer 4C deviates from the experimental measurement. The energy of isomer 4D is much higher than the most stable structure (4A). Therefore, isomers 4C and 4D probably do not exist in our experiments. According to our theoretical calculations, the most stable structure of Al_2VO_2 neutral show a V-shape structure arranged in the order of Al–O–V–O–Al , which is somewhat similar to the V-shape structure of Al_3O_2 ^{41,43,50}. However, the $\angle\text{OVO}$ angle in Al_2VO_2 is about 169° , much bigger than the $\angle\text{OAIO}$ angle in Al_3O_2 .

4.5. Al_3VO_2^- . The lowest-energy isomer of Al_3VO_2^- (5A) can also be considered to be evolved from isomer 2B with the second and third Al atoms bonding to the bridging O atoms. It is a planar structure with C_{2v} symmetry. Isomer 5B can be generally obtained by adding one more Al atom to the O atom of isomer 4A or 4B. Isomer 5C is 0.26 eV higher than isomer 5A in energy. It is also a planar structure but with the V atom exchanging position with one of the side Al atoms. The ADEs and VDEs of 5A and 5C agree well with the experimental results. The VDEs of isomers 5B and 5D deviate more from the experimental measurements, indicating that isomers 5B and 5D probably do not exist in our experiments. It might be possible that one or both of isomers 5A and 5C are populated in the experiments. The most stable structure of Al_3VO_2 neutral is similar to that of Al_3VO_2^- except that the $\angle\text{AIOAl}$ angles in the neutral are smaller than those in the anion by approximately 30° . The reported ground-state structure of Al_4O_2 ^{47,50} is very close to that of Al_3VO_2 .

Both our experimental and theoretical results show that the ADEs and VDEs of AlVO_y^- ($y = 1-3$) clusters increase with the increasing degree of oxidation. From the most stable structures of the AlVO_y^- ($y = 2-3$) and Al_xVO_2^- ($x = 2-3$) clusters anion and their neutrals, it is found that there are more O atoms interacting with the V atom than with the Al atom. That is probably because the V–O interaction is stronger than the Al–O interaction as the dissociation energy of V–O bond (6.44 ± 0.2 eV) is larger than that of Al–O bond (5.26 ± 0.1 eV).⁶⁰ It has been reported that there are three types of V–O bonds in V_2O_5 solid depending on the coordination of the O atoms.⁶¹ For the O atom bonds to only one V atom, the V–O bond is a typical double bond²⁸ with bond length at ~ 1.58 Å; for the O atom bridging two V atoms, the V–O bond length is about 1.77 Å; for the O atom coordinated to three V atoms, the longest V–O bond length is about 2.02 Å. We also found similar V–O bonds in small aluminum–vanadium oxide clusters. For example, in AlVO_2 (isomer 2A') and AlVO_3 (isomer 3A') (Figure 4), the V–O bonds formed by the V atoms and terminal O atoms are 1.60 and 1.59 Å, respectively, while the V–O bonds formed by the V atoms and bridging O atoms are between 1.82–1.85 Å. In Al_3VO_2 (isomer 5A'), the V–O bond is about 2.02 Å since each O atoms coordinated to three metal atoms (two Al and one V).

5. Conclusions

We conducted a photoelectron spectroscopy study of small aluminum–vanadium oxide clusters, AlVO_y^- ($y = 1-3$) and Al_xVO_2^- ($x = 2-3$), and investigated the structural and bonding properties of these clusters and their corresponding neutrals by density functional calculations. The most probable structures of these clusters were tentatively assigned by comparing the theoretical VDEs with the experiment values. The structure of AlVO^- is proposed to be quasilinear with the O atom between the Al and V atoms. For AlVO_2^- , an irregular chain structure of Al–O–V–O and a C_{2v} cyclic structure might coexist. The most stable structure of AlVO_3^- cluster has the third O atom bending out of the plane of the four-membered AlVO_2 ring. Al_2VO_2^- has two nearly degenerate Al–O–V–O–Al chain structures that can be considered as cis and trans forms. Al_3VO_2^- also has two low-lying isomers containing a four-membered ring. The calculated low-lying structures of the anionic and neutral clusters reveal that more O atoms bonding to the V atom benefits the stability of the oxide clusters.

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