

# A photoelectron spectroscopic study of monovanadium oxide anions ( $\text{VO}_x^-$ , $x=1-4$ )

Hongbin Wu and Lai-Sheng Wang

Department of Physics, Washington State University, Richland, Washington 99352 and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352

(Received 3 September 1997; accepted 30 December 1997)

We report on a photoelectron spectroscopic study of monovanadium oxides,  $\text{VO}_x^-$  ( $x=1-4$ ), at four photon energies: 532, 355, 266, and 193 nm. Vibrationally resolved spectra are obtained for  $\text{VO}^-$  at 532 and 355 nm detachment photon energies. Two new low-lying excited states are observed for VO at 5630 and 14 920  $\text{cm}^{-1}$  above the ground state. These states are assigned to two doublet states,  $^2\Sigma^-$  and  $^2\Phi$ , respectively. The 532 and 355 nm spectra of  $\text{VO}_2^-$  reveal a single vibrational progression for the ground state with a frequency of 970  $\text{cm}^{-1}$  ( $\nu_1$ ). Three electronic excited states are observed for  $\text{VO}_2$  in the 193 nm spectrum. For  $\text{VO}_3^-$ , three surprisingly sharp detachment transitions are observed at 193 nm. The two excited states of  $\text{VO}_3$  are measured to be 0.59 and 0.79 eV above the ground state. The spectra of  $\text{VO}_2^-$  and  $\text{VO}_3^-$  are interpreted using the molecular-orbital schemes obtained in a recent *ab initio* theoretical study [Knight, Jr. *et al.*, J. Chem. Phys. **105**, 10237 (1996)], which predicts that both  $\text{VO}_2$  and  $\text{VO}_3$  neutrals are of  $C_{2v}$  symmetry with a doublet ground state. The spectrum of  $\text{VO}_4^-$  is obtained at 193 nm, showing features similar to that of  $\text{VO}_3^-$ , but much more broadened. The adiabatic electron affinities of VO,  $\text{VO}_2$ ,  $\text{VO}_3$ , and  $\text{VO}_4$  are measured to be 1.229 (8), 2.03 (1), 4.36 (5), and 4.0 (1) eV, respectively, with a significant increase from  $\text{VO}_2$  to  $\text{VO}_3$ . The electronic and geometrical structures of the series of monovanadium oxide species are discussed based on the current observation and previous spectroscopic and theoretical results. © 1998 American Institute of Physics. [S0021-9606(98)01813-3]

## I. INTRODUCTION

Transition metal oxides are of interest from both an experimental and theoretical point of view. Experimentally, properties of the metal–oxygen bond are crucial for the understanding of the chemisorptive and catalytic properties of metal oxides. Particularly, vanadium oxides are of considerable importance in catalysis and the investigation of the vanadium–oxygen chemical bonding would be highly valuable. Theoretically, molecules containing transition metals have been rather challenging due to the open *d* shells. Simple transition metal oxide molecules provide ideal systems for accurate theoretical treatments, and experimental spectroscopic information on these systems will be important in this endeavor.

Except for the VO molecule, very few studies have been carried out on the  $\text{VO}_x$  molecules. Vanadium monoxide is very important in astrophysics, because it is the second in abundance after TiO in the spectra of metal-rich M-type stars and has been extensively studied.<sup>1-9</sup> The ground state of VO is known to be a quartet state ( $X^4\Sigma^-$ ).<sup>7</sup> The  $X^4\Sigma^- - A^4\Pi$ ,  $X^4\Sigma^- - B^4\Pi$ , and  $X^4\Sigma^- - C^4\Sigma^-$  band systems have been observed for VO from the stellar spectra at 1055, 790, and 574 nm, respectively. Recently, lifetime measurements of the  $A^4\Pi$ ,  $B^4\Pi$ , and  $C^4\Sigma^-$  electronic states were performed using population probing of resonant two-photon ionization in a molecular beam.<sup>6</sup> However, the excitation energies of doublet excited states are much less characterized even

though several emission systems involving doublet–doublet transitions have been observed and analyzed.<sup>2</sup> The quartet nature of the VO ground state prevents direct optical transitions between the ground state and any doublet excited states.

The  $\text{VO}_2^-$  and  $\text{VO}_3^-$  anions have been observed in the vapor of vanadium oxide at temperatures between 1200 and 1500 K.<sup>10</sup> The enthalpies of formation for  $\text{VO}_2^-$  and  $\text{VO}_3^-$  and the electron affinity (EA) of  $\text{VO}_2$  were estimated from the equilibrium constants. Recently, an electron spin resonance (ESR) study was reported on VO,  $\text{VO}_2$ , and  $\text{VO}_3$  in neon matrix at 4 K, in combination with an *ab initio* theoretical study.<sup>11</sup> The ESR study shows that  $\text{VO}_2$  has a  $C_{2v}$  structure with a  $^2A_1$  ground state. The  $\text{VO}_3^-$  anion was suggested, from a HF-SCF calculation, to have a planar  $D_{3h}$  structure with a VO distance of 1.601 Å.<sup>12</sup> However, the recent *ab initio* calculation indicates that neutral  $\text{VO}_3$  has a  $C_{2v}$  symmetry, due to a Jahn–Teller distortion.<sup>11</sup> A superoxovanadium  $\text{VO}_4$  species was suggested to be observed in photo-oxidation of  $\text{V}(\text{CO})_6$  in low-temperature matrices.<sup>13</sup> While this work is in progress, a Fourier transform infrared (FTIR) matrix investigation has been reported for VO,  $\text{VO}_2$ ,  $\text{VO}_4$ , and  $\text{V}_2\text{O}_2$ .<sup>14</sup>

Bulk  $\text{VO}_2$  is a nonmagnetic insulator and a technologically important material. There is a phase transition at 341 K from rutile-type  $\text{VO}_2$  (a poor metal) to a monoclinic semiconductor. Since this phase transition is ultrafast,  $\text{VO}_2$  can be

used in optical switching devices, electrical switches, optical memory devices, bolometric-type light detectors, critical temperature sensors, and infrared spatial light modulators.<sup>15–18</sup> The  $\text{VO}_4$  unit in condensed phase has also attracted much attention because of its important role in oxovanadium catalysis.<sup>19</sup> In condensed phase, the pseudotetrahedral oxovanadium group has three basal-plane oxygens and a terminal, double-bonded oxygen. Recently, well-defined absorption, emission, and Raman spectra of the vanadium oxide species have revealed new electronic structure information for the pseudotetrahedral oxovanadium.<sup>20</sup>

The study of transition metal oxide species in the gas phase by photoelectron spectroscopy (PES) offers a unique opportunity to probe the electronic structure of the isolated molecules. Dyke *et al.* reported the first PES of neutral  $\text{VO}$ ,<sup>8</sup> and obtained information about the ground and excited states of  $\text{VO}^+$ .<sup>9</sup> We are most concerned with the electronic structure and spectroscopy of neutral species. Photodetachment PES of anions provides a unique technique for this purpose.<sup>21–29</sup> In this paper, we report the first systematic study on the monovanadium oxides,  $\text{VO}_x$  ( $x = 1–4$ ), and the determination of their EAs. For  $\text{VO}$ , we observe five low-lying excited states, including two new doublet states. For both  $\text{VO}_2$  and  $\text{VO}_3$ , we observe distinct low-lying excited states from the PES spectra of  $\text{VO}_2^-$  and  $\text{VO}_3^-$ , which are interpreted using the available *ab initio* calculations. Our PES spectrum of  $\text{VO}_4^-$  shows broad features, indicating a significant geometric change from the anion to the neutral. Our results provide electronic structure information on the isolated  $\text{VO}_x$  species and will be valuable to compare with future *ab initio* studies in order to thoroughly understand the V–O chemical bonding.

## II. EXPERIMENT

The  $\text{VO}_x^-$  species are generated by pulsed laser vaporization of a pure vanadium target into a pulsed helium carrier gas seeded with a small amount of  $\text{O}_2$ . The plasma reactions between the laser vaporized vanadium atoms and the oxygen form the  $\text{VO}_x^-$  species, which are entrained into the helium carrier gas and expanded through a 2 mm diameter nozzle into the source vacuum chamber to form a supersonic cluster beam.  $\text{VO}^-$  is produced more easily at the lowest  $\text{O}_2$  concentration, and a trace amount of oxygen on the surfaces of the target and the stainless steel nozzle is enough to produce abundant  $\text{VO}^-$ . If we use helium mixed with even 0.05%  $\text{O}_2$  as a carrier gas, the mass spectrum is dominated by the  $\text{VO}_2^-$  and  $\text{VO}_3^-$  species.

The magnetic-bottle time-of-flight (MTOF) photoelectron spectrometer used for this study has been described in detail previously.<sup>30,31</sup> Briefly, the negative clusters are extracted from the collimated cluster beam after one skimmer at  $90^\circ$  and are mass analyzed by a TOF mass spectrometer. The anions of interest are selected by a pulsed mass gate and decelerated by a momentum decelerator before crossing with a detachment laser beam in the MTOF interaction zone. The photoelectrons are collected by the magnetic-bottle at nearly 100% efficiency and are energy-analyzed by their time of flight in a 3.5 m long TOF tube. In the current work, a

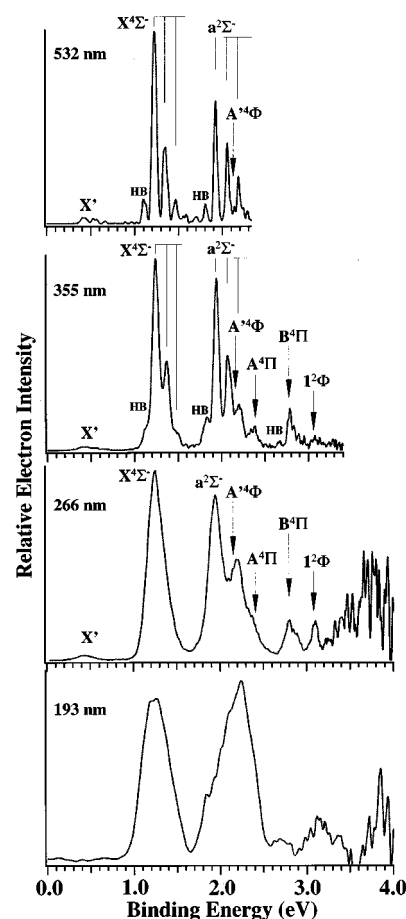


FIG. 1. Photoelectron spectra of  $\text{VO}^-$  at 532, 355, 266, and 193 nm. The 266 and 193 nm spectra are only plotted up to 4 eV binding energy, beyond which the spectra are rather noisy and contain no useful information. HB stands for hot band.

Q-switched Nd:YAG laser [532 nm (2.33 eV), 355 nm (3.49 eV), and 266 nm (4.66 eV)] and an ArF excimer laser [193 nm (6.42 eV)] are used for photodetachment. At 4.66 and 6.42 eV, spectra are taken at 20 Hz with the cluster beam off at alternating shots for background subtraction. The electron TOF spectra are converted to electron kinetic energy distributions, calibrated by the known spectra of  $\text{Cu}^-$ , and smoothed with a 5 meV square window function. The kinetic energy spectra are subtracted from the respective detachment photon energies to obtain the electron binding energy spectra presented. The resolution of the spectrometer is better than 30 meV at 1 eV kinetic energy. Therefore the best resolution is obtained when low photon energies are used. However, high photon energies allow more deeply bonded electrons to be probed and are necessary for clusters with high oxygen content due to their high EAs.

## III. RESULTS

Figure 1 shows the PES spectra of  $\text{VO}^-$  at four photon energies. The 532 nm spectrum exhibits two intense vibrational progressions ( $X$  and  $a$ ) with well-resolved vibrational structures and a very weak feature at low binding energy ( $X'$ ). Three more weak features beyond the 532 nm photon energy are revealed at the 355 nm spectrum. The feature at

TABLE I. Observed binding energies (BE) and spectroscopic constants for  $\text{VO}^-$  and  $\text{VO}$ .

	BE (eV)	Term value ( $\text{cm}^{-1}$ )		Vib. freq. ( $\text{cm}^{-1}$ )	
		This work	Previous <sup>a</sup>	This work	Previous <sup>b</sup>
$\text{VO}^- X'$	0.42(3)	6400(200)			
$X \ ^5\Pi(9\sigma^1 1\delta^2 4\pi^1)$		0		900(50)	
$\text{VO } X \ ^4\Sigma^-(9\sigma^1 1\delta^2)$	1.229(8) <sup>c</sup>	0		980(60)	1001.8
$a \ ^2\Sigma^-(9\sigma^1 1\delta^2)$	1.927(8)	5630(80)		1090(80)	
$A' \ ^4\Phi_{3/2}(9\sigma^1 1\delta^1 4\pi^1)$	2.1		6996.8		936.5
$\ ^4\Phi_{5/2}$			7171.4		
$\ ^4\Phi_{7/2}$			7342.7		
$\ ^4\Phi_{9/2}$			7509.0		
$A \ ^4\Pi_{-1/2}(9\sigma^1 1\delta^1 4\pi^1)$	2.395(8)	9400(80)	9449.7		884
$\ ^4\Pi_{1/2}$			9477.8		
$\ ^4\Pi_{3/2}$			9512.4		
$\ ^4\Pi_{5/2}$			9555.5		
$B \ ^4\Pi_{-1/2}(1\delta^2 4\pi^1)$	2.780(9)	12500(90)	12518.3		901
$\ ^4\Pi_{1/2}$			12571.7		
$\ ^4\Pi_{3/2}$			12637.1		
$\ ^4\Pi_{5/2}$			12711.9		
$1 \ ^2\Phi(9\sigma^1 1\delta^1 4\pi^1)$	3.079(15)	14920(90)			

<sup>a</sup>From Ref. 2.<sup>b</sup>From Ref. 1.<sup>c</sup>Adiabatic electron affinity of  $\text{VO}$ .

3.079 eV is shown more clearly in the 266 nm spectrum, which also seems to reveal more transitions at higher binding energies, but no definitive assignments can be made due to the poor signal-to-noise ratio. The vibrational progression of the  $a$  band is observed to exhibit remarkable changes at 266 nm: the intensity of the  $\nu=1$  peak is decreased while that of the  $\nu=2$  peak is strongly enhanced. Such intensity changes suggest that there may be overlapping electronic states whose detachment cross sections are dependent on photon energies. The 193 nm spectrum supports this suggestion and shows even more dramatic intensity changes in the region of the  $a$  band, even though the resolution and count rate are poor at 193 nm. The weak feature at the low binding energy ( $X'$ ) is most likely due to an electronic excited state of the  $\text{VO}^-$  anion. HB in Fig. 1 represents the hot band transitions due to the vibrationally excited states of the  $\text{VO}^-$  anion, shown most clearly in the 532 nm spectrum. The binding energies of the observed electronic states and the obtained spectroscopic constants are listed in Table I. The assignments will be discussed below.

Figure 2 shows the PES spectra of  $\text{VO}_2^-$  at four photon energies. The 532 nm spectrum displays a simple vibrational progression ( $X$ ). There is also a weak feature ( $X'$ ) and a broad unresolved feature ( $X''$ ) at the low binding energy side. The 355 nm spectrum shows an extra, albeit weak and broad, feature ( $A$ ) at the high binding energy side beyond the energy range accessible in the 532 nm detachment energy. The intensity of this feature ( $A$ ) seems to be enhanced in the 266 nm spectrum, which reveals yet another feature ( $B$ ) at the high binding energy side although the statistics of this feature are poor due to the presence of noise in the high binding energy range. The intensities of the  $A$  and  $B$  features appear to become even stronger in the 193 nm spectrum,

which reveals yet another feature ( $C$ ) at the high binding energy side. Thus from 532 to 193 nm each higher photon energy reveals successively a higher binding energy feature. The resolution for the  $X$  feature is seen to deteriorate significantly from 532 to 193 nm due to the increasing electron kinetic energies. The  $X'$  and  $X''$  features become only shoulders in the high photon energy spectra. It is also interesting

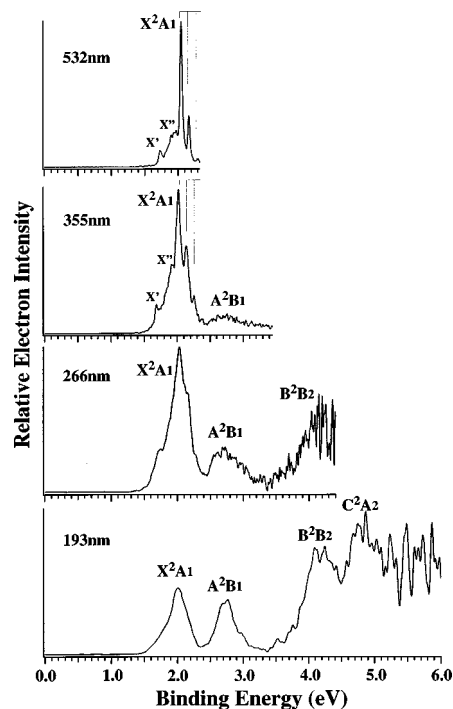
FIG. 2. Photoelectron spectra of  $\text{VO}_2^-$  at 532, 355, 266, and 193 nm.

TABLE II. Observed binding energies (BE) and spectroscopic constants for  $\text{VO}_2$  and  $\text{VO}_2^-$ .

	BE (eV)	Term value (eV)		Vib. freq. ( $\text{cm}^{-1}$ )	
		This work	Ref. 1	This work	Ref. 14
$\text{VO}_2^-$					
$X'$	1.72 (2)	0.31			
$X''$	$\sim 1.9$	$\sim 0.1$			
$X \ ^1A_1(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$					
$\text{VO}_2$					
$X \ ^2A_1(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	2.03 (1) <sup>a</sup>	0	0	970(40)	946.3
$A \ ^2B_1(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	2.6 (1)	0.6	1 <sup>b</sup>		
$B \ ^2B_2(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	4.0 (1)	2.0	2.0 <sup>c</sup>		
$C \ ^2A_2(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	4.6 (1)	2.6	3.0 <sup>c</sup>		

<sup>a</sup>Adiabatic electron affinity of  $\text{VO}_2$ .

<sup>b</sup>Estimate from  $g$ -tensor analysis. The value from *ab initio* calculation is 0.3 eV (Ref. 11).

<sup>c</sup>Obtained from *ab initio* calculations (Ref. 11).

to observe that the intensity of the  $A$  feature shows such strong photon energy dependence. The  $X'$  and  $X''$  features, which show weak dependence on source conditions but cannot be quite completely eliminated, are attributed to excited states of the  $\text{VO}_2^-$  anion. The observed binding energies and spectroscopic constants are listed in Table II for  $\text{VO}_2$  and  $\text{VO}_2^-$ . The  $A$ ,  $B$ , and  $C$  bands are all quite broad without any resolved fine features and their binding energies can only be estimated. The detailed assignments of the  $\text{VO}_2^-$  spectra will be discussed below.

Figure 3 displays the PES spectra of  $\text{VO}_3^-$  at 266 and 193 nm, as well as the spectrum of  $\text{VO}_4^-$  at 193 nm. The  $\text{VO}_3^-$  anion exhibits such high binding energy that the 266 nm photon is barely enough to detach it and the 266 nm spectrum only shows an onset of the  $\text{VO}_3^-$  spectrum. At 193 nm, three rather surprisingly sharp and well separated detachment features are revealed. Because the  $\text{VO}_3^-$  anion can be produced rather abundantly, its PES spectrum is the easiest to take and gives the best signal-to-noise ratio at 193 nm. The  $\text{VO}_4^-$  anion can be produced but with much less abun-

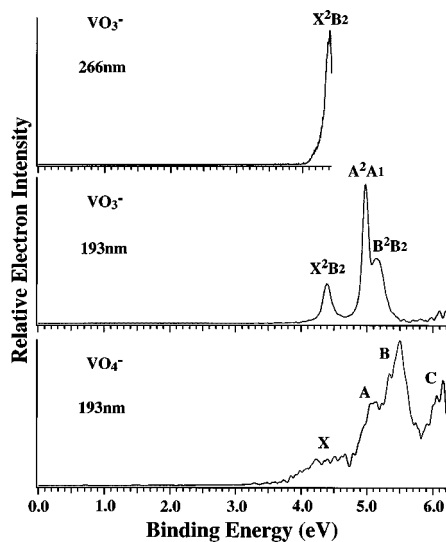


FIG. 3. Photoelectron spectra of  $\text{VO}_3^-$  at 266 and 193 nm, and of  $\text{VO}_4^-$  at 193 nm.

dance compared to  $\text{VO}_3^-$ . Thus the  $\text{VO}_4^-$  spectrum shows poorer signal-to-noise ratio, displaying four rather broad features ( $X, A, B, C$ ).  $\text{VO}_4^-$  also has very high electron binding energies similar to  $\text{VO}_3^-$ . The  $X$ ,  $A$ , and  $B$  features of  $\text{VO}_4^-$  seem to be similar to the three features of  $\text{VO}_3^-$ . The observed binding energies for  $\text{VO}_3^-$  and  $\text{VO}_4^-$  are summarized in Table III. The binding energies for  $\text{VO}_4^-$  can only be estimated due to the broad nature of the spectrum. Figure 4 summarizes and compares all the spectra for  $\text{VO}_x^-$  ( $x = 1-4$ ). In the following, we will discuss each species in detail.

## IV. DISCUSSION

### A. VO and $\text{VO}^-$

VO is one of the better studied transition metal monoxide molecules after TiO due to its importance in astrophysics. Its electronic structure and spectroscopy are relatively well known and have been reviewed by Merer in 1989 along with other diatomic  $3d$  transition metal oxides.<sup>1</sup> It has also been investigated in several theoretical studies.<sup>7</sup> The ground state of VO is well established to be a quartet state,  $X \ ^4\Sigma^-$ , with an electronic configuration of  $3\pi^4 8\sigma^2 9\sigma^1 1\delta^2$ , where the three unpaired electrons predominantly occupy the bonding  $4s(\sigma)$  and nonbonding  $3d(\delta)$  molecular orbitals. Due to the quartet nature of the VO ground state, the low-lying quartet states of VO are well known, including the  $A' \ ^4\Phi$  and  $A \ ^4\Pi(9\sigma^1 1\delta^1 4\pi^1)$ ,  $B \ ^4\Pi(1\delta^2 4\pi^1)$ ,  $C \ ^4\Sigma^-(1\delta^2 10\sigma^1)$ , and  $D \ ^4\Delta(9\sigma^1 1\delta^1 10\sigma^1)$  states.<sup>1-6</sup> The many low-lying doublet states, however, are not known due to the forbidden optical transitions between the quartet and the doublet states. The lowest known excited state for VO is the  $A' \ ^4\Phi_{3/2}$  state at  $6996.8 \text{ cm}^{-1}$  above the ground state.<sup>2</sup> However, our observed lowest excited state in the  $\text{VO}^-$  PES spectrum is the progression starting at 1.927 eV (Fig. 1), which gives an excitation energy of  $5630 \text{ cm}^{-1}$  (Table I), much lower than the known lowest quartet state ( $A' \ ^4\Phi_{3/2}$ ).

The ground state of the  $\text{VO}^-$  anion is not known. The extra electron in the anion can either enter the  $4\pi$ ,  $9\sigma$ , or  $1\delta$  orbital to give a configuration of  $3\pi^4 8\sigma^2 9\sigma^1 1\delta^2 4\pi^1$ ,  $3\pi^4 8\sigma^2 9\sigma^2 1\delta^2$ , or  $3\pi^4 8\sigma^2 9\sigma^1 1\delta^3$ , respectively. The third

TABLE III. Observed binding energies (BE) and spectroscopic constants for VO<sub>3</sub> and VO<sub>4</sub>.

		BE (eV)	Term values (eV)
VO <sub>3</sub> <sup>-</sup>	X <sup>1</sup> A <sub>1</sub> (6b <sub>2</sub> <sup>2</sup> 12a <sub>1</sub> <sup>2</sup> 7b <sub>2</sub> <sup>2</sup> )		
VO <sub>3</sub>	X <sup>2</sup> B <sub>2</sub> (6b <sub>2</sub> <sup>2</sup> 12a <sub>1</sub> <sup>2</sup> 7b <sub>2</sub> <sup>1</sup> )	4.36(5) <sup>a</sup>	0
	A <sup>2</sup> A <sub>1</sub> (6b <sub>2</sub> <sup>2</sup> 12a <sub>1</sub> <sup>1</sup> 7b <sub>2</sub> <sup>2</sup> )	4.95 (5)	0.59(5)
	B <sup>2</sup> B <sub>2</sub> (6b <sub>2</sub> <sup>1</sup> 12a <sub>1</sub> <sup>2</sup> 7b <sub>2</sub> <sup>2</sup> )	5.15 (5)	0.79(5)
VO <sub>4</sub>	X	4.0 (1) <sup>b</sup>	0
	A	5.0 (1)	1.0 (1)
	B	5.4 (1)	1.4 (1)
	C	6.0 (1)	2.0 (1)

<sup>a</sup>Adiabatic electron affinity of VO<sub>3</sub>.<sup>b</sup>Estimated adiabatic electron affinity of VO<sub>4</sub>.

configuration can be eliminated based on two observations. First, the occupation of the 1δ orbital loses the exchange energy which is known to be important.<sup>7</sup> This makes the occupation of the 1δ orbital unfavorable. Second, the 1δ orbital is nonbonding and the PES of the VO neutral gives a single 0–0 transition without any Franck–Condon factors (FCFs) for the higher vibrational levels when the 1δ orbital is ionized.<sup>8</sup> We expect that the detachment of the 1δ electron should similarly yield a single 0–0 peak. However, the first PES band of VO<sup>-</sup> shows a vibrational progression with significant FCFs for the higher vibrational levels, suggesting that there is a bond-length change between the anion and the neutral ground state. The occupation of the 9σ orbital can also be eliminated. This orbital is a bonding one and its occupation has been shown to enhance the VO bonding as in the <sup>2</sup>Δ(9σ<sup>2</sup>1δ<sup>1</sup>) state, which has a bond length even shorter than the VO ground state.<sup>2</sup> The VO<sup>-</sup> anion is more weakly bonded than the neutral ground state, as suggested by the smaller vibrational frequency of the anion (Table I). Therefore the only reasonable occupation of the extra electron in VO<sup>-</sup> is in the 4π orbital, giving a X<sup>5</sup>Π(3π<sup>4</sup>8σ<sup>2</sup>9σ<sup>1</sup>1δ<sup>2</sup>4π<sup>1</sup>) state. This is also consistent with the ground-state configuration of CrO, which is isoelectronic to VO<sup>-</sup> and has a vibrational frequency similar to that of VO<sup>-</sup>.<sup>1</sup>

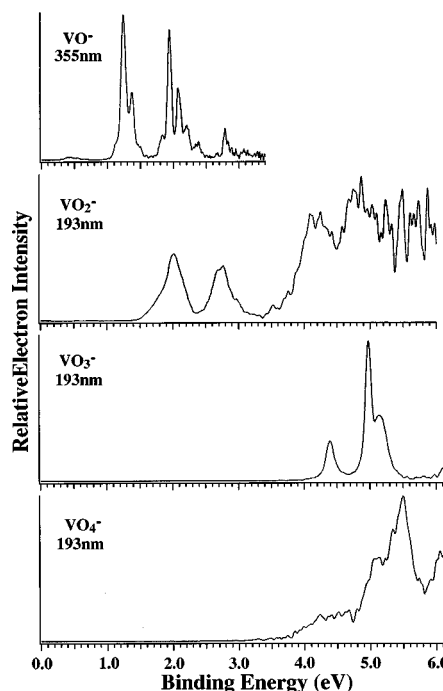
Having established the ground state of VO<sup>-</sup>, we can proceed to assign the features in Fig. 1. Three detachment channels are expected and can result in many low-lying excited states as follows:

$$3\pi^4 8\sigma^2 9\sigma^1 1\delta^2 4\pi^1 (X^5\Pi) \rightarrow 3\pi^4 8\sigma^2 9\sigma^1 1\delta^2: \quad {}^4\Sigma^-, {}^2\Sigma^-, {}^2\Gamma, {}^2\Sigma^+, \quad (1)$$

$$\rightarrow 3\pi^4 8\sigma^2 9\sigma^1 1\delta^1 4\pi^1: \quad {}^4\Phi, {}^4\Pi, {}^2\Phi(2), {}^2\Pi(2), \quad (2)$$

$$\rightarrow 3\pi^4 8\sigma^2 1\delta^2 4\pi^1: \quad {}^4\Pi, {}^2\Pi(2), {}^2H, {}^2\Phi. \quad (3)$$

Among these states, all the quartet states have been well characterized and should be easy to assign in principle. Among the doublets, only the <sup>2</sup>Σ<sup>+</sup> state from (1) is known. The <sup>4</sup>Σ<sup>-</sup> state, the ground state of the neutral VO, results from removing the single 4π electron in the anion. The 0–0 transition in the PES spectra yields an EA of 1.229 eV for VO and the observed vibrational frequency agrees well with

FIG. 4. Comparison of the evolution of the photoelectron spectra of VO<sub>x</sub><sup>-</sup> (x=1–4).

the known value of VO (Table I). As pointed out above, the first excited state observed in our PES spectra at 5630 cm<sup>-1</sup> does not agree with the known lowest quartet state, A' <sup>4</sup>Φ from (2). We assign this state as the <sup>2</sup>Σ<sup>-</sup> state, arising from the same electron configuration as the ground quartet state. The prominent vibrational progression is similar to that of the ground state, as expected, except that the vibrational frequency of the <sup>2</sup>Σ<sup>-</sup> state appears to be slightly higher (Table I). The A' <sup>4</sup>Φ state with its four spin-orbit components should occur between the v=1 and 2 peak of the a<sup>2</sup>Σ<sup>-</sup> state and may overlap slightly with these two peaks, complicating the definitive observation of the A' <sup>4</sup>Φ state. Further complication derives from the fact that the A' <sup>4</sup>Φ state has very low intensity at the low detachment photon energies where the resolutions are high. The small feature in between the v=1 and 2 peaks of the a<sup>2</sup>Σ<sup>-</sup> state in the 532 nm spectrum is due to the A' <sup>4</sup>Φ state. However, its appearance is more prominent at the 266 and 193 nm spectra where its intensity is significantly enhanced, distorting the vibrational progression of the a<sup>2</sup>Σ<sup>-</sup> state.

The weak feature at 2.4 eV of the 355 nm spectrum (Fig. 1) gives an excitation energy of 9400 cm<sup>-1</sup>, which is consistent with the position of the A <sup>4</sup>Π state from (2) (Table I). Its intensity is also enhanced at the 266 and 193 nm spectra, consistent with detaching a δ electron. The feature observed at 2.78 eV is assigned to the B <sup>4</sup>Π state due to the detachment of the single 9σ electron. The derived excitation energy of 12 500 cm<sup>-1</sup> is in excellent agreement with the known value of the B <sup>4</sup>Π state (Table I). A further higher energy feature, which is observed more prominently in the 266 nm spectrum (Fig. 1) is assigned to a <sup>2</sup>Φ state from (2). This feature has very low intensity at the 355 nm spectra and its intensity is enhanced with photon energy. This photon en-

ergy dependence is similar to that of the  $A' \ ^4\Phi$  and  $A \ ^4\Pi$  states, which are derived from the same configuration, and is consistent with detaching a  $\delta$  electron.

The weak feature at 0.42 eV, labeled as  $X'$  in Fig. 1, is likely due to detachment from an excited state of the  $\text{VO}^-$  anion to the  $\text{VO}$  ground state. Such an excited state of an anion has been observed previously in  $\text{CuO}^-$ .<sup>26</sup> The excited state in  $\text{VO}^-$  is about  $6400 \text{ cm}^{-1}$  above the ground state of  $\text{VO}^-$ .

## B. $\text{VO}_2$ and $\text{VO}_2^-$

Bulk  $\text{VO}_2$  has been extensively studied in the condensed phase. However, studies on the isolated  $\text{VO}_2$  molecule are scarce. Recently Knight *et al.* reported a combined ESR and *ab initio* study on the  $\text{VO}_2$  molecule in a low-temperature matrix.<sup>11</sup> Their study shows that  $\text{VO}_2$  is nonlinear with an unpaired electron predominantly occupying a vanadium  $3d$ -type orbital, giving a  $X \ ^2A_1$  ground state. Their calculation also yields a  $\angle\text{O}-\text{V}-\text{O}$  angle of  $110.5^\circ$  and a  $\text{V}-\text{O}$  bond length of  $1.653 \text{ \AA}$  with a  $C_{2v}$  symmetry. From the  $g$ -tensor analysis, they were able to deduce an  $A \ ^2B_1$  low-lying excited state for  $\text{VO}_2$  with about 1 eV excitation energy. Their calculation gives a value of 0.3 eV for the  $A \ ^2B_1$  excited state. The  $X \ ^2A_1$  and  $A \ ^2B_1$  states are considered to correlate with the  $^2\Delta$  state in a linear OVO case. They also predicted two more excited states correlating with the  $^2\Pi$  state of the linear OVO case. These two states are calculated to be 2.0 eV ( $B \ ^2B_2$ ) and 3.0 eV ( $C \ ^2A_2$ ) above the  $X \ ^2A_1$  ground state. The uncertainty in the calculations was expected to be  $\pm 0.3$  eV. Chertihin *et al.* have just published a matrix FTIR experiment on  $\text{VO}_2$ .<sup>14</sup> They estimated a  $\angle\text{O}-\text{V}-\text{O}$  angle of  $118 \pm 3^\circ$  and measured the  $\nu_1$  and  $\nu_3$  vibrational frequencies to be  $946.3$  and  $935.9 \text{ cm}^{-1}$ , respectively. In an earlier mass spectrometry experiment, Rudnyi *et al.* measured the enthalpy of formation of  $\text{VO}_2^-$  and estimated the EA of  $\text{VO}_2$  to be  $2.3 \pm 0.2$  eV.<sup>10</sup> With the above information, we can analyze and understand the  $\text{VO}_2^-$  PES spectra shown in Fig. 2.

The occupied valence molecular orbitals of  $\text{VO}_2$  are  $8a_1^2 5b_2^2 1a_2^2 9a_1^2 3b_1^2 6b_2^2 10a_1^1$  ( $X \ ^2A_1$ ).<sup>11</sup> The  $10a_1$  orbital is primarily of  $\text{V } 3d$  character; all the other orbitals involve primarily the  $\text{O } 2p$  orbitals. The  $10a_1$  and  $3b_1$  orbitals correlate with the  $\delta$  orbital in the linear OVO and the  $1a_2$  and  $5b_2$  correlate with the  $\pi$  orbital in the linear OVO, as mentioned above. In the anion, most likely, the extra electron occupies the  $10a_1$  orbital, giving a closed-shell ground state for the  $\text{VO}_2^-$  anion ( $X \ ^1A_1$ ), consistent with its high enthalpy of formation and stability in the gas phase.<sup>10</sup> Then within the single particle approximation, detachment from each filled orbital of  $\text{VO}_2^-$  will yield one band in the PES spectrum which should be straightforward to interpret.

As shown in Fig. 2, the 532 nm spectrum of  $\text{VO}_2^-$  exhibits a well-resolved vibrational progression with a frequency of  $970 \text{ cm}^{-1}$ , which is in good agreement with the  $\nu_1$  frequency ( $946.3 \text{ cm}^{-1}$ ) measured for  $\text{VO}_2$  in the matrix FTIR experiment.<sup>14</sup> This progression corresponds to the ground state ( $X \ ^2A_1$ ) of  $\text{VO}_2$  and is due to the detachment of a  $10a_1$  electron. The  $\nu_1$  vibrational progression suggests that

there is a slight  $\text{V}-\text{O}$  bond-length change between the anion and neutral ground state. Very little bending vibration is observed as seen from the sharp  $\nu_1$  peaks (the bending vibration would broaden the  $\nu_1$  peaks since its frequency is probably too small to be resolved), suggesting that there is little  $\text{O}-\text{V}-\text{O}$  angle change between the anion and neutral ground state. This is consistent with the nature of the  $10a_1$  orbital, which is of mainly  $3d$  character. The 0-0 transition at 2.03(1) eV defines the adiabatic EA for  $\text{VO}_2$ , suggesting that the EA estimated previously was inaccurate and too high.<sup>10</sup>

Besides the main vibrational progression, there are more features at the low binding energy side in the 532 nm spectrum. These are possibly due to hot band transitions, but cannot be attributed to hot bands entirely since similar sequence bands are not observed on the high binding energy side. Therefore we attribute these features to be from electronic excited states of the  $\text{VO}_2^-$  anion. The lowest binding energy feature at 1.72 eV is quite sharp, yielding an excitation energy of 0.31 eV for the anion excited state. A similar electronic excited state of the anion has been observed in  $\text{VO}^-$ , as seen in Fig. 1. The low binding energy features could also be due to  $\text{V}(\text{O}_2)^-$  complexes. Similar  $\text{M}(\text{O}_2)^-$  complexes are common for the late transition metal atoms.<sup>22,28</sup> However, this kind of complex seems to be less likely for the early transition metals due to the strong  $\text{M}-\text{O}$  bonding. For example, the  $\text{V}(\text{O}_2)$  complex was not observed in the previous matrix studies.<sup>11,14</sup> Therefore we think that the features that we observe are more likely to be due to electronic excited states of the  $\text{OVO}^-$  anion.

In the higher photon energy spectra of  $\text{VO}_2^-$  (Fig. 2), three more features are revealed, which are due to the detachment of deeper valence orbitals and correspond to excited states of the  $\text{VO}_2$  molecule. All these higher energy features show broadbands without any resolved vibrational structure, suggesting that there are significant geometry changes between the anion ground state and the excited states of  $\text{VO}_2$ . These changes are most likely in the  $\angle\text{O}-\text{V}-\text{O}$  bond angle such that the  $\nu_2$  mode is active, leading to the broad detachment bands. The bond angle change is consistent with the fact that all these features are due to detachment from orbitals involving the  $\text{O}2p$ . It is interesting to observe that the second detachment band near 2.6 eV shows very strong photon energy dependence. We assign this feature to the  $A \ ^2B_1$  state, as suggested in the previous ESR experiment.<sup>11</sup> Our estimate of 0.6 eV for the excitation energy is in reasonable agreement with that found in the ESR experiment. The  $A \ ^2B_1$  state is due to the detachment of an electron from the  $3b_1$  orbital of  $\text{VO}_2^-$ . The enhancement of the detachment cross section with photon energy for this detachment channel is consistent with the fact that the  $3b_1$  orbital corresponds to a component of the  $\delta$  orbital in the linear OVO case.<sup>32</sup> We assign the two higher energy features at 4.0 and 4.6 eV to the two excited states,  $B \ ^2B_2$  and  $C \ ^2A_2$ , respectively, as predicted in the previous *ab initio* calculations.<sup>11</sup> The overall assignments are shown in Fig. 2 and Table II. The calculated excitation energies for the  $B \ ^2B_2$  and  $C \ ^2A_2$  states are surprisingly in good agreement with our experimental estimates. The  $B \ ^2B_2$  and  $C \ ^2A_2$  states are due to detachment from the  $5b_2$  and  $1a_2$  orbitals,

respectively, suggesting that the molecular-orbital ordering, as given in the previous calculation, needs to be changed to the following:  $8a_1^2 5b_2^2 9a_1^2 1a_2^2 6b_2^2 3b_1^2 10a_1^1$  if the calculated excited states are correct. However, calculations of excited states are known to be rather difficult. Our assignments of the excited states according to the existing calculations should probably be viewed as tentative, pending confirmation by more accurate calculations.

### C. VO<sub>3</sub> and VO<sub>3</sub><sup>-</sup>

The electron binding energy of VO<sub>3</sub><sup>-</sup> is observed to increase dramatically compared to that of VO<sub>2</sub><sup>-</sup>. We obtain an adiabatic EA of 4.36 eV for VO<sub>3</sub>, which is more than twice as much as that of VO<sub>2</sub> (Tables II and III). The 266 nm spectrum of VO<sub>3</sub><sup>-</sup> only reveals a fairly narrow peak due to the detachment transition to the ground state of VO<sub>3</sub> without any resolved vibrational structure (Fig. 3). The 193 nm spectrum of VO<sub>3</sub><sup>-</sup> shows two more features at binding energies of 4.95 and 5.15 eV. All the three detachment transitions in VO<sub>3</sub><sup>-</sup> give fairly sharp features, suggesting that the VO<sub>3</sub><sup>-</sup> anion and VO<sub>3</sub> neutral both have very similar geometries. The narrow features in the VO<sub>3</sub><sup>-</sup> spectra are in sharp contrast to those in the VO<sub>2</sub><sup>-</sup> spectra (Fig. 4), where both stretching and bending vibrations are shown to be active.

The high EA of VO<sub>3</sub> can be easily understood because the V atom only has five valence electrons and the additional electron in the anion will make VO<sub>3</sub><sup>-</sup> a closed-shell molecule, thus stabilizing the extra electron. This suggests that VO<sub>3</sub> is open-shell with an unpaired electron which is most likely on the O atoms. The above observation is consistent with the recent ESR experiment by Knight *et al.*<sup>11</sup> They observed an ESR signal which shows a <sup>51</sup>V hyperfine splitting about ten times smaller than that in VO<sub>2</sub> and tentatively attributed it to VO<sub>3</sub>. Their *ab initio* calculations support the assignment to VO<sub>3</sub>, yielding a planar (C<sub>2v</sub>) VO<sub>3</sub> with an unpaired electron (a <sup>2</sup>B<sub>2</sub> ground state). The calculations show that VO<sub>3</sub> has a short V–O bond (1.576 Å) along the C<sub>2</sub> symmetry axis and two equivalent longer V–O bonds (1.677 Å) off the C<sub>2</sub> axis with a smaller ∠O–V–O angle of 110.6°. The unpaired electron in the X <sup>2</sup>B<sub>2</sub> ground state of VO<sub>3</sub> is predicted to occupy a molecular orbital (7b<sub>2</sub>) of mainly 2p<sub>z</sub> character on the two off-axis O atoms. In the anion, the extra electron enters into the 7b<sub>2</sub> orbital to give the closed shell VO<sub>3</sub><sup>-</sup> (<sup>1</sup>A<sub>1</sub>) anion. Therefore only the bending vibration involving the two off-axis O atoms is expected to be active in the detachment of a 7b<sub>2</sub> electron. This is consistent with our observation of the first detachment feature (X <sup>2</sup>B<sub>2</sub>, Fig. 3), showing no V–O stretching vibration which would be easily resolvable. Any bond angle change between the anion and neutral is likely to be rather small since no extensive bending vibration is observed as indicated by the rather narrow detachment peak (X <sup>2</sup>B<sub>2</sub>).

The next two molecular orbitals of VO<sub>3</sub>, as given by the *ab initio* calculations, are 12a<sub>1</sub> and 6b<sub>2</sub> which are both of mainly O2p character. We assign the two higher binding energy features in the PES spectrum of VO<sub>3</sub><sup>-</sup> to the detachment of an electron from these two orbitals, respectively, giving the two low-lying excited states of VO<sub>3</sub>: A <sup>2</sup>A<sub>1</sub> and

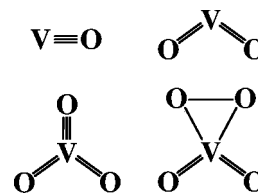


FIG. 5. Schematic structures of the VO<sub>x</sub> (x=1–4) species.

B <sup>2</sup>B<sub>2</sub>, as shown in Fig. 3 and Table III. It is surprising that the A and B detachment features are also rather sharp with little resolved vibrational excitation, meaning that there are no significant geometry changes between the VO<sub>3</sub><sup>-</sup> anion and the two excited states of VO<sub>3</sub>. This suggests that VO<sub>3</sub> is a rather rigid and stable molecule. There is very little known about the VO<sub>3</sub> molecule except the work by Knight *et al.*<sup>11</sup> VO<sub>3</sub><sup>-</sup> was observed in the previous mass spectrometric work,<sup>10</sup> but the VO<sub>3</sub> molecule was not observed in the recent FTIR experiment of V+O<sub>2</sub>.<sup>14</sup> Our results suggest that the VO<sub>3</sub><sup>-</sup> anion is also likely to have a C<sub>2v</sub> structure, the same as the neutral. This is in contrast to the previous HF-SCF calculation which suggests that the VO<sub>3</sub><sup>-</sup> anion has a planar D<sub>3h</sub> structure.<sup>12</sup>

### D. VO<sub>4</sub> and VO<sub>4</sub><sup>-</sup>

Surface-dispersed vanadium oxide catalysts are composed of pseudotetrahedral VO<sub>4</sub> oxovanadium groups (–O<sub>3</sub>V=O), whose electronic structure has been extensively investigated and debated due to its important role in catalysis.<sup>20</sup> It has a C<sub>3v</sub> structure with a terminal V=O bond; the three basal O atoms are bonded to the substrates. The isolated VO<sub>4</sub> species has never been observed in the gas phase and is unlikely to adopt the C<sub>3v</sub> structure as on the surfaces. In two previous matrix IR experiments,<sup>13,14</sup> the VO<sub>4</sub> species has been observed and proposed to contain a VO<sub>2</sub> unit and a peroxy-O<sub>2</sub>(η<sup>2</sup>) unit (Fig. 5). The IR experiments show that the OVO angle of the VO<sub>2</sub> unit in this VO<sub>4</sub> species is nearly identical to that in VO<sub>2</sub> itself.

The V atom has five valence electrons and the VO<sub>4</sub> species is O-excess or electron-deficient. We have studied similar O-excess oxide species previously, such as in FeO<sub>4</sub>,<sup>24</sup> CuO<sub>3</sub>,<sup>26</sup> and Al<sub>2</sub>O<sub>5</sub>.<sup>27</sup> In these O-excess metal oxide species, the peroxy unit is very common to accommodate the additional O atoms, and all exhibit very high EAs. We observe that the VO<sub>4</sub> species behaves similarly. The PES spectrum of VO<sub>4</sub><sup>-</sup> is similar to that of VO<sub>3</sub><sup>-</sup>, but much broader. Our estimated EA of about 4.0 eV for VO<sub>4</sub> is quite high, suggesting that the valence molecular orbital where the extra electron resides in VO<sub>4</sub><sup>-</sup> is most likely composed of the O2p-type orbitals similar to that in VO<sub>3</sub><sup>-</sup>. The broad features observed in the VO<sub>4</sub><sup>-</sup> PES spectrum indicate that there are significant geometry changes between VO<sub>4</sub><sup>-</sup> and VO<sub>4</sub>, in particular, the VO<sub>4</sub> ground state which gives a very broad band ranging from about 3.9 to 4.7 eV (X in Fig. 4 of the VO<sub>4</sub><sup>-</sup> spectrum). The VO<sub>4</sub><sup>-</sup> anion has been proposed to contain a peroxy-O<sub>2</sub> (η<sup>2</sup>-O<sub>2</sub>) (Fig. 5) unit while the VO<sub>4</sub> neutral contains a superoxy-O<sub>2</sub>(σ-O<sub>2</sub>) unit where the O<sub>2</sub> is tilted and only one of the O atoms is bonded to V.<sup>13</sup> This proposal is entirely

consistent with our broad detachment feature for the  $X$  ground state of  $\text{VO}_4$ . The  $A$ ,  $B$ , and  $C$  features in the  $\text{VO}_4^-$  spectrum correspond to detachment of more tightly bound electrons. The estimated binding energies for the four detachment features of  $\text{VO}_4^-$  are summarized in Table III. Their detailed assignments will have to await future theoretical calculations.

### E. Electronic and structural evolution from VO to $\text{VO}_4$

Vanadium has four principal oxides: VO,  $\text{V}_2\text{O}_3$ ,  $\text{V}_2\text{O}_4$ , and  $\text{V}_2\text{O}_5$  with oxidation states of vanadium ranging from +2 to +5.<sup>33</sup> The maximum oxidation state of +5 originates from the five valence electrons of the V atom. The chemical bonding between V and O is extremely strong with both covalent and ionic characters.<sup>7</sup> We can view the series from VO to  $\text{VO}_3$  as a sequential oxidation in which the oxidation state of V increases from +2 in VO to +5 in  $\text{VO}_3$ .  $\text{VO}_3$  is interesting because six electrons are needed to saturate the valences of the O atoms, making  $\text{VO}_3^-$  a closed-shell species with an extremely high electron binding energy. The numbers of unpaired electrons in the  $\text{VO}_x$  species correlate with this trend, with three in VO and one in  $\text{VO}_2$  all on the V atom. The ESR experiment shows that  $\text{VO}_3$  also has an unpaired electron, but mostly on the O atoms.<sup>11</sup> In  $\text{VO}_4$ , there are not enough valence electrons so that the molecule contains a superoxo  $\sigma\text{-O}_2$  unit.<sup>13,14</sup> In the condensed phase, the  $\text{VO}_4$  unit is very common, but it has a  $-3$  formal charge state as  $\text{VO}_4^{3-}$ .<sup>34</sup> Therefore the V–O interactions involve strong ionic bonding character.

The structures of the  $\text{VO}_x$  series of species are also interesting. The VO diatomic has a bond length of 1.589 Å and is viewed theoretically as a triple bond due to strong  $\pi$  interactions between the O long pair and the empty  $d$  orbitals on the V atom.<sup>7</sup> As obtained from *ab initio* calculations by Knight *et al.*,<sup>11</sup> the  $\text{VO}_2$  molecule has a  $C_{2v}$  structure with a V–O bond length of 1.653 Å and  $\angle\text{O–V–O}$  angle of 110.5°. The V–O bond length in  $\text{VO}_2$  is longer than that in the VO diatomic and can be viewed as a  $\text{V}=\text{O}$  double bond. Most interesting are the structures of  $\text{VO}_3$  and  $\text{VO}_4$ , both containing a  $\text{VO}_2$  unit nearly identical with that of  $\text{VO}_2$  itself in terms of both the V–O bond length and  $\angle\text{O–V–O}$  bond angle. The axial V–O bond length in  $\text{VO}_3$ , as obtained by Knight *et al.* is 1.576 Å,<sup>11</sup> which is even shorter than that in the VO diatomic, indicating the axial V–O bond can be characterized as a triple bond. The off-axis V–O bonds are shown to have a bond length of 1.667 Å and a  $\angle\text{O–V–O}$  angle of 110.6°, almost the same as in  $\text{VO}_2$  itself. Our PES spectrum suggests that the  $\text{VO}_3^-$  anion has nearly identical geometry to the neutral. The  $\text{VO}_3^-$  anion has been suggested to have a planar  $D_{3h}$  structure,<sup>12</sup> which is not consistent with our observation that there is little geometry change between the anion and the neutral. In  $\text{VO}_4$ , the  $\text{O}_2$  unit can replace either the triple bonded O or one of the double-bonded O atoms. The matrix IR spectrum of  $\text{VO}_4$  shows that the  $\text{VO}_4$  molecule contains a  $\text{VO}_2$  unit nearly identical to that of  $\text{VO}_2$  itself,<sup>14</sup> suggesting that the  $\text{O}_2$  unit in  $\text{VO}_4$  replaces the triple-bonded O atom in  $\text{VO}_3$ . The structures of the  $\text{VO}_x$  ( $x=1-4$ ) species are schematically summarized in Fig. 5. This series

of oxide molecules exhibits rather interesting and unusual structural and bonding properties. More systematic *ab initio* theoretical studies seem to be warranted.

### V. CONCLUSIONS

In conclusion, we have reported the first PES spectra for a series of monovanadium oxide species,  $\text{VO}_x^-$  ( $x=1-4$ ). We have obtained the electron affinities and direct spectroscopic and electronic structure information for the corresponding neutral species. For the  $\text{VO}^-$ , the PES spectra reveal two low-lying doublet electronic states that are not known from previous optical spectroscopy. Vibrationally resolved spectra are obtained for the ground state of  $\text{VO}_2$ . Three low-lying excited states of  $\text{VO}_2$  are measured directly from the PES spectra of  $\text{VO}_2^-$ . A surprisingly simple PES spectrum is measured for  $\text{VO}_3^-$ , showing three rather sharp transitions. A very high EA for  $\text{VO}_3$  is obtained as expected from the closed-shell nature of  $\text{VO}_3^-$ . The spectra of  $\text{VO}_2^-$  and  $\text{VO}_3^-$  are interpreted using previous *ab initio* calculations for the  $\text{VO}_2$  and  $\text{VO}_3$  neutrals, which are predicted to have  $C_{2v}$  structures. Our PES results imply that the  $\text{VO}_2^-$  and  $\text{VO}_3^-$  anions also have  $C_{2v}$  structures similar to the neutrals. The  $\text{VO}_4$  molecule is also shown to have a rather high EA and the spectrum of  $\text{VO}_4^-$  shows similarities to that of  $\text{VO}_3^-$ , but is much more broadened. The electronic and geometrical structures of the series of  $\text{VO}_x$  oxide species exhibit an interesting trend and more systematic and accurate *ab initio* calculations would be desirable to completely understand these simple monovanadium oxide species.

### ACKNOWLEDGMENTS

This work is supported by the U.S. National Science Foundation (CHE-9404428) and performed at Pacific Northwest National Laboratory operated by Battelle for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. L.-S.W. is an Alfred P. Sloan Research Fellow.

- <sup>1</sup>A. J. Merer, *Annu. Rev. Phys. Chem.* **40**, 407 (1989).
- <sup>2</sup>A. J. Merer, G. Huang, A. S.-C. Cheung, and A. W. Taylor, *J. Mol. Spectrosc.* **125**, 465 (1987).
- <sup>3</sup>G. Huang, A. J. Merer, and D. J. Clouthier, *J. Mol. Spectrosc.* **153**, 32 (1992).
- <sup>4</sup>A. G. Adam, M. Barnes, B. Berno, R. D. Bower, and A. J. Merer, *J. Mol. Spectrosc.* **170**, 94 (1995).
- <sup>5</sup>A. S.-C. Cheung, P. G. Hajigeorgiou, G. Huang, S.-Z. Huang, and A. J. Merer, *J. Mol. Spectrosc.* **163**, 443 (1994).
- <sup>6</sup>L. Karlsson, B. Lindgren, C. Lundevall, and U. Sassenberg, *J. Mol. Spectrosc.* **181**, 274 (1997).
- <sup>7</sup>E. G. Bakalbassis, M. D. Stiakaki, A. C. Tsipis, and C. A. Tsipis, *Chem. Phys.* **205**, 389 (1996); M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *J. Chem. Phys.* **86**, 2123 (1987); C. W. Bauschlicher, Jr. and S. R. Langhoff, *ibid.* **85**, 5936 (1986); C. W. Bauschlicher, Jr. and P. Maitre, *Theor. Chim. Acta* **90**, 189 (1985).
- <sup>8</sup>J. M. Dyke, B. W. J. Gravenor, M. P. Hastings, and A. Morris, *J. Phys. Chem.* **89**, 4613 (1985).
- <sup>9</sup>E. A. Carter and W. A. Goddard III, *J. Phys. Chem.* **92**, 2109 (1988); E. Broclawik, *Int. J. Quantum Chem.* **56**, 779 (1995).
- <sup>10</sup>E. B. Rudnyi, E. A. Kaibicheva, and L. N. Sidorov, *J. Chem. Thermodyn.* **25**, 929 (1993).
- <sup>11</sup>L. B. Knight, Jr., R. Babb, M. Ray, T. J. Banisaukas III, L. Russon, R. S. Dailey, and E. R. Davidson, *J. Chem. Phys.* **105**, 10237 (1996).
- <sup>12</sup>F. Ramondo, L. Bencivenni, N. Sanna, and S. N. Cesaro, *J. Mol. Struct.: THEOCHEM* **253**, 121 (1992).

- <sup>13</sup>M. J. Almond and R. W. Atkins, *J. Chem. Soc. Dalton Trans.* **835**, (1994).
- <sup>14</sup>G. V. Chertihin, W. D. Bare, and L. Andrews, *J. Phys. Chem. A* **101**, 5090 (1997).
- <sup>15</sup>L. A. Gea, L. A. Boatner, J. D. Budai, and R. A. Zuhr, in *Ion-Solid Interactions for Materials Modification and Processing*, edited by D. B. Poker, D. Ila, Y.-T. Cheng, L. R. Harriott, and T. W. Sigmon (Materials Research Society, Boston, 1995), pp. 215.
- <sup>16</sup>D. Yin, N. Xu, J. Zhang, and X. Zheng, *J. Phys. D* **29**, 1051 (1996).
- <sup>17</sup>V. L. Gal'perin, I. A. Khakhaev, F. A. Chudnovskii, and E. B. Shadrin, *Sov. Tech. Phys. Lett.* **18**, 329 (1992).
- <sup>18</sup>C. E. Lee, R. A. Atkins, W. N. Gibler, and H. F. Taylor, *Appl. Opt.* **28**, 4511 (1991).
- <sup>19</sup>S. T. Oyama, *Res. Chem. Inter.* **15**, 165 (1991); G. C. Bond and S. F. Tahir, *Appl. Catal.* **71**, 1 (1991).
- <sup>20</sup>K. Tran, M. A. Hanning-Lee, A. Biswas, A. E. Stiegman, and G. W. Scott, *J. Am. Chem. Soc.* **117**, 2618 (1995).
- <sup>21</sup>P. C. Engelking and W. C. Lineberger, *J. Chem. Phys.* **66**, 5054 (1977).
- <sup>22</sup>H. Wu, S. R. Desai, and L. S. Wang, *J. Chem. Phys.* **103**, 4363 (1995).
- <sup>23</sup>L. S. Wang, H. Wu, S. R. Desai, and L. Lou, *Phys. Rev. B* **53**, 8028 (1996).
- <sup>24</sup>H. Wu, S. R. Desai, and L. S. Wang, *J. Am. Chem. Soc.* **118**, 5296 (1996).
- <sup>25</sup>L. S. Wang, H. Wu, and S. R. Desai, *Phys. Rev. Lett.* **76**, 4853 (1996).
- <sup>26</sup>H. Wu, S. R. Desai, and L. S. Wang, *J. Phys. Chem. A* **101**, 2103 (1997).
- <sup>27</sup>S. R. Desai, H. Wu, C. Rohfling, and L. S. Wang, *J. Chem. Phys.* **106**, 1309 (1997).
- <sup>28</sup>H. Wu and L. S. Wang, *J. Chem. Phys.* **107**, 16 (1997).
- <sup>29</sup>H. Wu and L. S. Wang, *J. Chem. Phys.* **107**, 8221 (1997).
- <sup>30</sup>L. S. Wang, H. S. Cheng, and J. Fan, *J. Chem. Phys.* **102**, 9480 (1995).
- <sup>31</sup>L. S. Wang and H. Wu in *Advances in Metal and Semiconductor Clusters. Vol. 4: Cluster Materials*, edited by M. A. Duncan (JAI, Greenwich, CT, 1997).
- <sup>32</sup>Detachment cross sections for orbitals with high angular momenta are expected to increase with photon energies. See S. Hufner, *Photoelectron Spectroscopy* (Springer-Verlag, New York, 1995), p. 15.
- <sup>33</sup>F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed. (Wiley, New York, 1988).
- <sup>34</sup>A. V. Kondratenko, E. S. Fomin, K. M. Neiman, and V. A. Nasluzov, *Opt. Spectrosc.* **66**, 195 (1989); P. J. A. Ribeiro-Claro, A. M. Amado, and J. J. C. Teixeira-Dias, *J. Comp. Chem.* **17**, 1183 (1996).