

A photoelectron spectroscopic study of monovanadium oxide anions (VO_x^- , $x=1-4$)

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We report on a photoelectron spectroscopic study of monovanadium oxides, VO_x^- ($x=1-4$), at four photon energies: 532, 355, 266, and 193 nm. Vibrationally resolved spectra are obtained for VO^- at 532 and 355 nm detachment photon energies. Two new low-lying excited states are observed for VO at 5630 and 14 920 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 VO_2^- reveal a single vibrational progression for the ground state with a frequency of 970 cm^{-1} (ν_1). Three electronic excited states are observed for VO_2 in the 193 nm spectrum. For VO_3^- , three surprisingly sharp detachment transitions are observed at 193 nm. The two excited states of VO_3 are measured to be 0.59 and 0.79 eV above the ground state. The spectra of VO_2^- and 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 VO_2 and VO_3 neutrals are of C_{2v} symmetry with a doublet ground state. The spectrum of VO_4^- is obtained at 193 nm, showing features similar to that of VO_3^- , but much more broadened. The adiabatic electron affinities of VO, VO_2 , VO_3 , and 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 VO_2 to 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 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.¹⁻⁹ The ground state of VO is known to be a quartet state ($X^4\Sigma^-$).⁷ 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.⁶ 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.² The quartet nature of the VO ground state prevents direct optical transitions between the ground state and any doublet excited states.

The VO_2^- and VO_3^- anions have been observed in the vapor of vanadium oxide at temperatures between 1200 and 1500 K.¹⁰ The enthalpies of formation for VO_2^- and VO_3^- and the electron affinity (EA) of VO_2 were estimated from the equilibrium constants. Recently, an electron spin resonance (ESR) study was reported on VO, VO_2 , and VO_3 in neon matrix at 4 K, in combination with an *ab initio* theoretical study.¹¹ The ESR study shows that VO_2 has a C_{2v} structure with a 2A_1 ground state. The 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.¹² However, the recent *ab initio* calculation indicates that neutral VO_3 has a C_{2v} symmetry, due to a Jahn–Teller distortion.¹¹ A superoxovanadium VO_4 species was suggested to be observed in photo-oxidation of $\text{V}(\text{CO})_6$ in low-temperature matrices.¹³ While this work is in progress, a Fourier transform infrared (FTIR) matrix investigation has been reported for VO, VO_2 , VO_4 , and V_2O_2 .¹⁴

Bulk VO_2 is a nonmagnetic insulator and a technologically important material. There is a phase transition at 341 K from rutile-type VO_2 (a poor metal) to a monoclinic semiconductor. Since this phase transition is ultrafast, 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.^{15–18} The VO_4 unit in condensed phase has also attracted much attention because of its important role in oxovanadium catalysis.¹⁹ 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.²⁰

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 VO ,⁸ and obtained information about the ground and excited states of VO^+ .⁹ We are most concerned with the electronic structure and spectroscopy of neutral species. Photodetachment PES of anions provides a unique technique for this purpose.^{21–29} In this paper, we report the first systematic study on the monovanadium oxides, VO_x ($x = 1–4$), and the determination of their EAs. For VO , we observe five low-lying excited states, including two new doublet states. For both VO_2 and VO_3 , we observe distinct low-lying excited states from the PES spectra of VO_2^- and VO_3^- , which are interpreted using the available *ab initio* calculations. Our PES spectrum of 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 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 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 O_2 . The plasma reactions between the laser vaporized vanadium atoms and the oxygen form the 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. VO^- is produced more easily at the lowest 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 VO^- . If we use helium mixed with even 0.05% O_2 as a carrier gas, the mass spectrum is dominated by the VO_2^- and VO_3^- species.

The magnetic-bottle time-of-flight (MTOF) photoelectron spectrometer used for this study has been described in detail previously.^{30,31} Briefly, the negative clusters are extracted from the collimated cluster beam after one skimmer at 90° 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

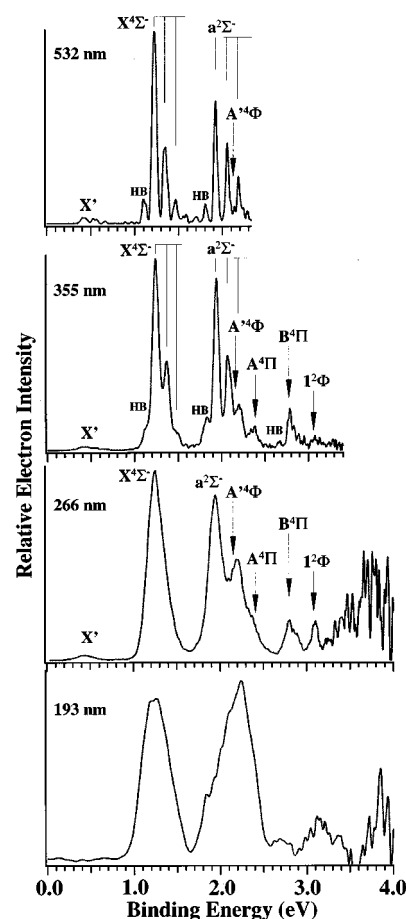


FIG. 1. Photoelectron spectra of VO^- at 532, 355, 266, and 193 nm. The 266 and 193 nm spectra are only plotted up to 4 eV binding energy, beyond which the spectra are rather noisy and contain no useful information. HB stands for hot band.

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 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 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 VO^- and VO.

	BE (eV)	Term value (cm^{-1})		Vib. freq. (cm^{-1})	
		This work	Previous ^a	This work	Previous ^b
$\text{VO}^- X'$	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) ^c	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)			

^aFrom Ref. 2.^bFrom Ref. 1.^cAdiabatic electron affinity of 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 VO^- anion. HB in Fig. 1 represents the hot band transitions due to the vibrationally excited states of the 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 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

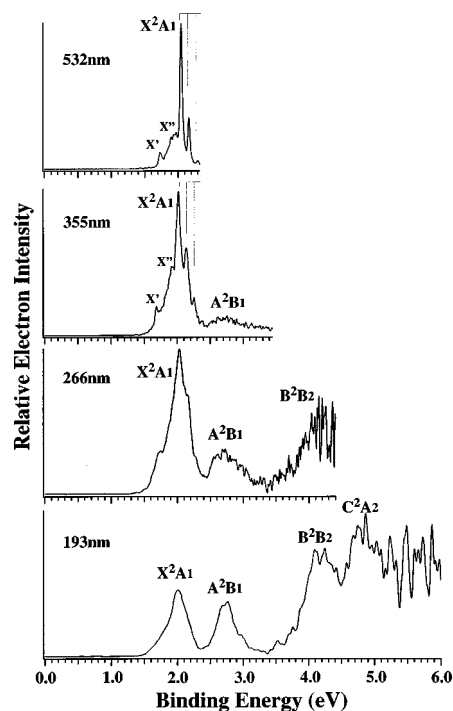
FIG. 2. Photoelectron spectra of VO_2^- at 532, 355, 266, and 193 nm.

TABLE II. Observed binding energies (BE) and spectroscopic constants for VO_2 and VO_2^- .

	BE (eV)	Term value (eV)		Vib. freq. (cm^{-1})	
		This work	Ref. 1	This work	Ref. 14
VO_2^-					
X'	1.72 (2)	0.31			
X''	~ 1.9	~ 0.1			
$X \ ^1A_1(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$					
VO_2					
$X \ ^2A_1(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	2.03 (1) ^a	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 ^b		
$B \ ^2B_2(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	4.0 (1)	2.0	2.0 ^c		
$C \ ^2A_2(1a_2^2 6b_2^2 3b_1^2 10a_1^2)$	4.6 (1)	2.6	3.0 ^c		

^aAdiabatic electron affinity of VO_2 .

^bEstimate from g -tensor analysis. The value from *ab initio* calculation is 0.3 eV (Ref. 11).

^cObtained 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 VO_2^- anion. The observed binding energies and spectroscopic constants are listed in Table II for VO_2 and 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 VO_2^- spectra will be discussed below.

Figure 3 displays the PES spectra of VO_3^- at 266 and 193 nm, as well as the spectrum of VO_4^- at 193 nm. The 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 VO_3^- spectrum. At 193 nm, three rather surprisingly sharp and well separated detachment features are revealed. Because the 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 VO_4^- anion can be produced but with much less abun-

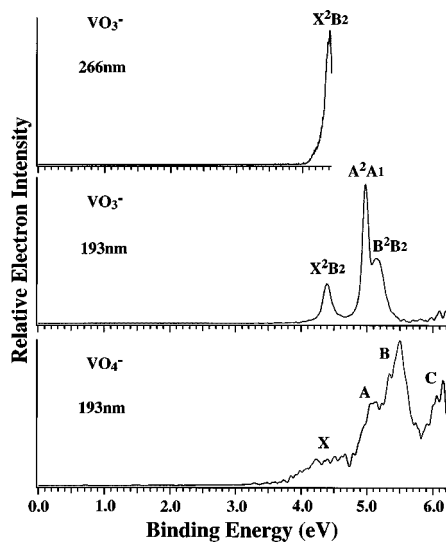


FIG. 3. Photoelectron spectra of VO_3^- at 266 and 193 nm, and of VO_4^- at 193 nm.

dance compared to VO_3^- . Thus the VO_4^- spectrum shows poorer signal-to-noise ratio, displaying four rather broad features (X, A, B, C). VO_4^- also has very high electron binding energies similar to VO_3^- . The X , A , and B features of VO_4^- seem to be similar to the three features of VO_3^- . The observed binding energies for VO_3^- and VO_4^- are summarized in Table III. The binding energies for VO_4^- can only be estimated due to the broad nature of the spectrum. Figure 4 summarizes and compares all the spectra for VO_x^- ($x = 1-4$). In the following, we will discuss each species in detail.

IV. DISCUSSION

A. VO and 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.¹ It has also been investigated in several theoretical studies.⁷ 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.¹⁻⁶ 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 cm^{-1} above the ground state.² However, our observed lowest excited state in the VO^- PES spectrum is the progression starting at 1.927 eV (Fig. 1), which gives an excitation energy of 5630 cm^{-1} (Table I), much lower than the known lowest quartet state ($A' \ ^4\Phi_{3/2}$).

The ground state of the VO^- anion is not known. The extra electron in the anion can either enter the 4π , 9σ , or 1δ 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 VO₃ and VO₄.

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

^aAdiabatic electron affinity of VO₃.^bEstimated adiabatic electron affinity of VO₄.

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.⁷ 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.⁸ We expect that the detachment of the 1δ electron should similarly yield a single 0–0 peak. However, the first PES band of VO⁻ 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 ²Δ(9σ²1δ¹) state, which has a bond length even shorter than the VO ground state.² The VO⁻ 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⁻ is in the 4π orbital, giving a X⁵Π(3π⁴8σ²9σ¹1δ²4π¹) state. This is also consistent with the ground-state configuration of CrO, which is isoelectronic to VO⁻ and has a vibrational frequency similar to that of VO⁻.¹

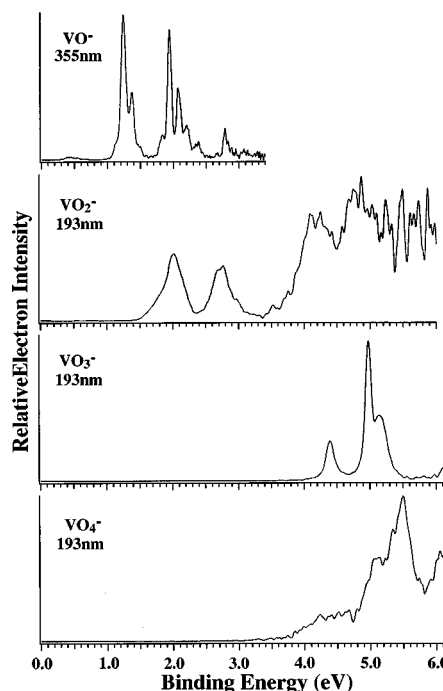
Having established the ground state of VO⁻, we can proceed to assign the features in Fig. 1. Three detachment channels are expected and can result in many low-lying excited states as follows:

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

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

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

Among these states, all the quartet states have been well characterized and should be easy to assign in principle. Among the doublets, only the ²Σ⁺ state from (1) is known. The ⁴Σ⁻ 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_x⁻ (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⁻¹ does not agree with the known lowest quartet state, A' ⁴Φ from (2). We assign this state as the ²Σ⁻ 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 ²Σ⁻ state appears to be slightly higher (Table I). The A' ⁴Φ state with its four spin-orbit components should occur between the v=1 and 2 peak of the a²Σ⁻ state and may overlap slightly with these two peaks, complicating the definitive observation of the A' ⁴Φ state. Further complication derives from the fact that the A' ⁴Φ 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 a²Σ⁻ state in the 532 nm spectrum is due to the A' ⁴Φ 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 a²Σ⁻ state.

The weak feature at 2.4 eV of the 355 nm spectrum (Fig. 1) gives an excitation energy of 9400 cm⁻¹, which is consistent with the position of the A ⁴Π 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 ⁴Π state due to the detachment of the single 9σ electron. The derived excitation energy of 12 500 cm⁻¹ is in excellent agreement with the known value of the B ⁴Π state (Table I). A further higher energy feature, which is observed more prominently in the 266 nm spectrum (Fig. 1) is assigned to a ²Φ 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 δ 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 VO^- anion to the VO ground state. Such an excited state of an anion has been observed previously in CuO^- .²⁶ The excited state in VO^- is about 6400 cm^{-1} above the ground state of VO^- .

B. VO_2 and VO_2^-

Bulk VO_2 has been extensively studied in the condensed phase. However, studies on the isolated VO_2 molecule are scarce. Recently Knight *et al.* reported a combined ESR and *ab initio* study on the VO_2 molecule in a low-temperature matrix.¹¹ Their study shows that 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° and a $\text{V}-\text{O}$ bond length of 1.653 \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 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 ± 0.3 eV. Chertihin *et al.* have just published a matrix FTIR experiment on VO_2 .¹⁴ They estimated a $\angle\text{O}-\text{V}-\text{O}$ angle of $118 \pm 3^\circ$ and measured the ν_1 and ν_3 vibrational frequencies to be 946.3 and 935.9 cm^{-1} , respectively. In an earlier mass spectrometry experiment, Rudnyi *et al.* measured the enthalpy of formation of VO_2^- and estimated the EA of VO_2 to be 2.3 ± 0.2 eV.¹⁰ With the above information, we can analyze and understand the VO_2^- PES spectra shown in Fig. 2.

The occupied valence molecular orbitals of VO_2 are $8a_1^2 5b_2^2 1a_2^2 9a_1^2 3b_1^2 6b_2^2 10a_1^1$ ($X \ ^2A_1$).¹¹ 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 δ orbital in the linear OVO and the $1a_2$ and $5b_2$ correlate with the π 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 VO_2^- anion ($X \ ^1A_1$), consistent with its high enthalpy of formation and stability in the gas phase.¹⁰ Then within the single particle approximation, detachment from each filled orbital of 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 VO_2^- exhibits a well-resolved vibrational progression with a frequency of 970 cm^{-1} , which is in good agreement with the ν_1 frequency (946.3 cm^{-1}) measured for VO_2 in the matrix FTIR experiment.¹⁴ This progression corresponds to the ground state ($X \ ^2A_1$) of VO_2 and is due to the detachment of a $10a_1$ electron. The ν_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 ν_1 peaks (the bending vibration would broaden the ν_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 VO_2 , suggesting that the EA estimated previously was inaccurate and too high.¹⁰

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 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 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.^{22,28} 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.^{11,14} Therefore we think that the features that we observe are more likely to be due to electronic excited states of the OVO^- anion.

In the higher photon energy spectra of 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 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 VO_2 . These changes are most likely in the $\angle\text{O}-\text{V}-\text{O}$ bond angle such that the ν_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.¹¹ 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 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 δ orbital in the linear OVO case.³² 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.¹¹ 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. VO₃ and VO₃⁻

The electron binding energy of VO₃⁻ is observed to increase dramatically compared to that of VO₂⁻. We obtain an adiabatic EA of 4.36 eV for VO₃, which is more than twice as much as that of VO₂ (Tables II and III). The 266 nm spectrum of VO₃⁻ only reveals a fairly narrow peak due to the detachment transition to the ground state of VO₃ without any resolved vibrational structure (Fig. 3). The 193 nm spectrum of VO₃⁻ shows two more features at binding energies of 4.95 and 5.15 eV. All the three detachment transitions in VO₃⁻ give fairly sharp features, suggesting that the VO₃⁻ anion and VO₃ neutral both have very similar geometries. The narrow features in the VO₃⁻ spectra are in sharp contrast to those in the VO₂⁻ spectra (Fig. 4), where both stretching and bending vibrations are shown to be active.

The high EA of VO₃ can be easily understood because the V atom only has five valence electrons and the additional electron in the anion will make VO₃⁻ a closed-shell molecule, thus stabilizing the extra electron. This suggests that VO₃ 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.*¹¹ They observed an ESR signal which shows a ⁵¹V hyperfine splitting about ten times smaller than that in VO₂ and tentatively attributed it to VO₃. Their *ab initio* calculations support the assignment to VO₃, yielding a planar (C_{2v}) VO₃ with an unpaired electron (a ²B₂ ground state). The calculations show that VO₃ has a short V–O bond (1.576 Å) along the C₂ symmetry axis and two equivalent longer V–O bonds (1.677 Å) off the C₂ axis with a smaller ∠O–V–O angle of 110.6°. The unpaired electron in the X ²B₂ ground state of VO₃ is predicted to occupy a molecular orbital (7b₂) of mainly 2p_z character on the two off-axis O atoms. In the anion, the extra electron enters into the 7b₂ orbital to give the closed shell VO₃⁻ (¹A₁) anion. Therefore only the bending vibration involving the two off-axis O atoms is expected to be active in the detachment of a 7b₂ electron. This is consistent with our observation of the first detachment feature (X ²B₂, 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 ²B₂).

The next two molecular orbitals of VO₃, as given by the *ab initio* calculations, are 12a₁ and 6b₂ which are both of mainly O2p character. We assign the two higher binding energy features in the PES spectrum of VO₃⁻ to the detachment of an electron from these two orbitals, respectively, giving the two low-lying excited states of VO₃: A ²A₁ and

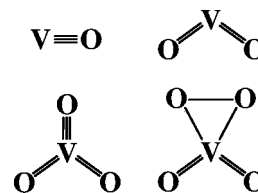


FIG. 5. Schematic structures of the VO_x (x=1–4) species.

B ²B₂, 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 VO₃⁻ anion and the two excited states of VO₃. This suggests that VO₃ is a rather rigid and stable molecule. There is very little known about the VO₃ molecule except the work by Knight *et al.*¹¹ VO₃⁻ was observed in the previous mass spectrometric work,¹⁰ but the VO₃ molecule was not observed in the recent FTIR experiment of V+O₂.¹⁴ Our results suggest that the VO₃⁻ anion is also likely to have a C_{2v} structure, the same as the neutral. This is in contrast to the previous HF-SCF calculation which suggests that the VO₃⁻ anion has a planar D_{3h} structure.¹²

D. VO₄ and VO₄⁻

Surface-dispersed vanadium oxide catalysts are composed of pseudotetrahedral VO₄ oxovanadium groups (–O₃V=O), whose electronic structure has been extensively investigated and debated due to its important role in catalysis.²⁰ It has a C_{3v} structure with a terminal V=O bond; the three basal O atoms are bonded to the substrates. The isolated VO₄ species has never been observed in the gas phase and is unlikely to adopt the C_{3v} structure as on the surfaces. In two previous matrix IR experiments,^{13,14} the VO₄ species has been observed and proposed to contain a VO₂ unit and a peroxo-O₂(η²) unit (Fig. 5). The IR experiments show that the OVO angle of the VO₂ unit in this VO₄ species is nearly identical to that in VO₂ itself.

The V atom has five valence electrons and the VO₄ species is O-excess or electron-deficient. We have studied similar O-excess oxide species previously, such as in FeO₄,²⁴ CuO₃,²⁶ and Al₂O₅.²⁷ In these O-excess metal oxide species, the peroxo unit is very common to accommodate the additional O atoms, and all exhibit very high EAs. We observe that the VO₄ species behaves similarly. The PES spectrum of VO₄⁻ is similar to that of VO₃⁻, but much broader. Our estimated EA of about 4.0 eV for VO₄ is quite high, suggesting that the valence molecular orbital where the extra electron resides in VO₄⁻ is most likely composed of the O2p-type orbitals similar to that in VO₃⁻. The broad features observed in the VO₄⁻ PES spectrum indicate that there are significant geometry changes between VO₄⁻ and VO₄, in particular, the VO₄ ground state which gives a very broad band ranging from about 3.9 to 4.7 eV (X in Fig. 4 of the VO₄⁻ spectrum). The VO₄⁻ anion has been proposed to contain a peroxo-O₂(η²-O₂) (Fig. 5) unit while the VO₄ neutral contains a superoxo-O₂(σ-O₂) unit where the O₂ is tilted and only one of the O atoms is bonded to V.¹³ This proposal is entirely

consistent with our broad detachment feature for the X ground state of VO_4 . The A , B , and C features in the VO_4^- spectrum correspond to detachment of more tightly bound electrons. The estimated binding energies for the four detachment features of 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 VO_4

Vanadium has four principal oxides: VO, V_2O_3 , V_2O_4 , and V_2O_5 with oxidation states of vanadium ranging from +2 to +5.³³ 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.⁷ We can view the series from VO to VO_3 as a sequential oxidation in which the oxidation state of V increases from +2 in VO to +5 in VO_3 . VO_3 is interesting because six electrons are needed to saturate the valences of the O atoms, making VO_3^- a closed-shell species with an extremely high electron binding energy. The numbers of unpaired electrons in the VO_x species correlate with this trend, with three in VO and one in VO_2 all on the V atom. The ESR experiment shows that VO_3 also has an unpaired electron, but mostly on the O atoms.¹¹ In VO_4 , there are not enough valence electrons so that the molecule contains a superoxo $\sigma\text{-O}_2$ unit.^{13,14} In the condensed phase, the VO_4 unit is very common, but it has a -3 formal charge state as VO_4^{3-} .³⁴ Therefore the V–O interactions involve strong ionic bonding character.

The structures of the 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 π interactions between the O long pair and the empty d orbitals on the V atom.⁷ As obtained from *ab initio* calculations by Knight *et al.*,¹¹ the 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 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 VO_3 and VO_4 , both containing a VO_2 unit nearly identical with that of 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 VO_3 , as obtained by Knight *et al.* is 1.576 Å,¹¹ 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 VO_2 itself. Our PES spectrum suggests that the VO_3^- anion has nearly identical geometry to the neutral. The VO_3^- anion has been suggested to have a planar D_{3h} structure,¹² which is not consistent with our observation that there is little geometry change between the anion and the neutral. In VO_4 , the O_2 unit can replace either the triple bonded O or one of the double-bonded O atoms. The matrix IR spectrum of VO_4 shows that the VO_4 molecule contains a VO_2 unit nearly identical to that of VO_2 itself,¹⁴ suggesting that the O_2 unit in VO_4 replaces the triple-bonded O atom in VO_3 . The structures of the 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, 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 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 VO_2 . Three low-lying excited states of VO_2 are measured directly from the PES spectra of VO_2^- . A surprisingly simple PES spectrum is measured for VO_3^- , showing three rather sharp transitions. A very high EA for VO_3 is obtained as expected from the closed-shell nature of VO_3^- . The spectra of VO_2^- and VO_3^- are interpreted using previous *ab initio* calculations for the VO_2 and VO_3 neutrals, which are predicted to have C_{2v} structures. Our PES results imply that the VO_2^- and VO_3^- anions also have C_{2v} structures similar to the neutrals. The VO_4 molecule is also shown to have a rather high EA and the spectrum of VO_4^- shows similarities to that of VO_3^- , but is much more broadened. The electronic and geometrical structures of the series of 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.

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