Identification, Structure, and Spectroscopy of Neutral Vanadium Oxide Clusters

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ABSTRACT

Neutral vanadium oxide clusters are studied by photoionization time of flight mass spectroscopy (TOFMS), electronic spectroscopy, and density functional theory (DFT) calculations.   Mass spectra of vanadium oxide clusters are observed by photoionization with lasers of three different wavelengths: 118 nm, 193 nm, and 355 nm.   Mechanisms of 118 nm single photon ionization and 193 nm and 355 nm multiphoton ionization/fragmentation of vanadium oxide clusters are discussed based on observed mass spectral patterns and linewidths of the mass spectral features.   Only the 118 nm laser light can ionize vanadium oxide neutral species by single photon ionization without fragmentation.   The stable vanadium oxide neutral clusters under saturated oxygen growth conditions are found to be of the form $(VO_2)_x (V_2O_5)_y$. Structures of the first few members of this series of clusters are determined through high level DFT calculations.   Fragmentation of this series of clusters through 355 and 193 nm multiphoton ionization processes is discussed in light of these calculated structures.   The $\widetilde{B}^2B_2 \longleftarrow \widetilde{X}^2A_1$ transition is observed for the VO_2 neutral species and ν_1 and ν_2 vibrations are assigned for both electronic states.   From this spectrum, the VO_2 rotational and vibrational temperatures are found to be ca. 50 and 700 K, respectively.

I. INTRODUCTION

Vanadium oxide catalysts are found throughout the chemical industry and synthesis laboratories. Nonetheless, the microscopic properties of specific local catalytic sites and the mechanism for catalytic activity of vanadium oxide catalysts remain unknown. The electronic and geometric structures of vanadium oxide gas phase clusters can correspond to condensed phase surface and/or defect structures and thus such clusters can have properties and behavior that relate or correspond to condensed phase chemical and physical phenomena. This local approach to condensed phase modeling was first articulated by Mutterties[1] and has since been explored by a number of other research groups[2].

Numerous studies of ionic vanadium oxide clusters ($V_mO_n^{\pm}$) have been reported.[3-13] Theoretical studies of the structures for ionic vanadium oxide clusters have been accomplished[3] and these structures have been employed to explore cluster ion reactivity.[3e] Experimentally, extensive mass spectroscopic and reaction studies have been reported for vanadium and vanadium oxide cations by the groups of Armentrout[4], Castleman[5] and Schwarz[6]. Photoelectron, zero electron kinetic energy (ZEKE), electronic, and infrared spectroscopic studies have been performed for ionic clusters by the groups of Hackett[7], Kaya[8], Leopold[9], Lineberger[10], Wang[11], Kondow[12], and Meijer[13].

Electronic spectroscopy of neutral metal oxide clusters is performed mainly by photoelectron spectroscopy for cluster anions in order to associate a spectrum with a given size cluster. A major difficulty for electronic spectroscopy of neutral clusters relates to the coexistence of many clusters in the gas phase simultaneously; a mass selective spectroscopic technique is required for a positive identification of the species carrying the observed spectrum. Cluster ionization is thereby required for the spectroscopic observation, but cluster fragmentation (loss of mass selectivity) is always a question. Nonetheless, electronic spectra for VO and V_2 have been reported.[14]

Mass spectrometric studies of neutral vanadium oxide clusters detected with photoionization are reported by Riley and coworkers[15] and Bernstein and coworkers[16]. In the former study, pure neutral V_n clusters are produced by laser ablation and expansion as a first step. These clusters are then passed into a flow tube reactor with O_2 gas and neutral V_mO_n clusters are generated. The V_mO_n clusters are ionized by either a 193 (ArF), 248 (KrF), or 308 (XeCl) nm laser, and detected and identified by time of flight (TOF) mass spectroscopy. In the latter study, neutral vanadium oxide clusters are produced by mixing the ablated metal plasma with an O_2 (0.1 to 6%) / He (99.9 to 94%) mixture directly, and expanding the subsequent mixture into a vacuum system. Neutral clusters in this experiment are ionized by low intensity 193 nm radiation; the observed mass spectra looks quite similar to those of ref. 15. Fielicke et al.[17] report infrared multiphoton dissociation spectra for vanadium oxide/ethylene cation clusters. They analyze fragmentation pathways through the wavelength dependence of the IR spectrum of ethylene for the observed fragment mass peaks.

Cluster fragmentation or loss of mass information during the ionization process required for detection is the motivating factor for the use of covariance mapping[16,18] analysis of mass spectra. A covariance mapping analysis of vanadium oxide mass spectra (193 nm ionization) shows a positive correlation between mass spectral features, implying, according to ref. 16, that the observed $V_mO_n^+$ clusters are related through a growth mechanism. In order not to lose information on the neutral cluster distribution, we have recently applied low energy/pulse (ca. 1 µJ), high energy/photon (10.5 eV, 118 nm) ionization for determination of the neutral cluster distribution of metal oxides.[19] 10.5 eV photons have sufficient energy to ionize almost all neutral metal oxide clusters[19,20]. [Note, however, that according to our calculations, VO_3 and VO_4, at ionization energies ca. 11.5 eV, may be exceptions to this generalization.]

Calculations have also been pursued for neutral vanadium oxide clusters at various levels of density functional[3a-d, 21a] and ab initio theory[3c,d, 21b]. Additionally, similations of

cluster reactivity and surface reactions have also been reported for this system.[22] V_2O_4 structures are reported by Pykavy et al.[3d] at the MR-ACPF/cc-pVQZ and B3LYP/cc-pVQZ levels.   Calatayud et al.[3a] also present data for this cluster at the UHF/6-31G* and B3LYP/6-31G* levels.   Refs. 3a and 3d get different lowest energy structures at these theory levels. Pykavy et al.[3d] calculated the structure of the lowest triplet state of V_2O_4 at the B3LYP and PB86/TZVP levels and finds a stable cis-ring structure only.   The energy difference between the cis-ring and trans-ring structures is small and calculational level dependent.   Calatayud et al.[3a] and Vyboishchikov et al.[21] find both ring and linear structures for V_2O_5 with the ring structures being more stable (20 kcal/mol) at the B3LYP/6-31G*, B3LYP, PB86/TZVP, DZP, and D(T)ZVP levels.   Justes et al.[3e] have calculated one of the structures for $V_4O_9^+$.

In the present study we apply 118, 355, and 193 nm laser light to ionize neutral vanadium oxide clusters in the gas phase.   The goal is to determine the neutral particle or "molecule" distribution present in the supersonic cluster beam.   This characterized neutral distribution of vanadium oxide species can then be employed to study reactions and properties of the generated species.   Of the three ionization wavelengths chosen for this study, only 118 nm single photon ionization can ionize the vanadium oxide clusters without fragmentation. Averaged TOF mass peak widths observed with 118 nm ionization are the same as the seeded Nd/YAG pulse time width (ca. 8 ns) and the individual ion peak widths are the same as the mass detector electron transit time (ca. 1.7 ns).   The observed V_mO_n mass spectra under these conditions are different for different O_2 content (0.1% to 6%) in the expansion gas.   Density functional theory calculations are employed to generate structures, energies, vibrations and excited electronic states for a number of the observed clusters.

We also obtain spectra for the $\tilde{B}^2B_2 \longleftarrow \tilde{X}^2A_1$ transition of vanadium dioxide VO_2.

The electronic transition can be detected at both the VO^+ and VO_2^+ mass channels.

Rotational and vibrational temperatures can be determined for VO_2 along with values of v_1 and

v_2 for both electronic states.

II.   EXPERIMENTAL PROCEDURES

The detailed experimental set up is given in earlier publications from this laboratory[16,19].

Briefly, vanadium oxide clusters are generated in a supersonic expansion into a vacuum system

by laser ablation of a metal foil into a flow of 0.1% to 6% O_2 in He at 100 psig.   The 0.25 mm

vanadium metal foil (99.7%) is purchased from Aldrich.   Clusters grow in high pressure

(probably ca. 10 psi) as the ablated metal plasma expands into the oxygen/helium mixture.

The temperature at which they grow is probably near the initial plasma temperature (ca. 3000

K).

The resulting clusters pass through an electric field region to remove ions created in the

metal ablation/metal oxide growth process.   Neutral vanadium oxide clusters pass through a 2

mm aperture skimmer into the ionization region of a time-of-flight mass spectrometer (Wiley-

McLauren design- R.M. Jordan Co.) and are ionized by one of three pulsed lasers: 193 nm, ArF;

355 nm, third harmonic of a seeded Nd/YAG 1.064 μm laser; or 118 nm, ninth harmonic of the

seeded Nd/YAG laser.   The 118 nm light is generated from the third harmonic of the seeded

Nd/YAG laser (~ 25 mJ/pulse, maximum energy), tripled in a Xe/Ar mixture at 1:10 relative

concentration for 200-500 torr total pressure.[19]

Synchronization of valve opening, lasers pulsing, and detection is accomplished by a

time delay generator.   TOFMS signals are monitored by a Galileo microchannel plate detector

(MCP) and acquired with a 500 MHz, 2 G sample/s Tektronix RTD 720 A transient digitizer

connected to a personal computer.   Each laser ionization pulse generates a full mass spectrum,

which is individually stored and saved in the computer before the next pulse arrives.

Averaged spectra are obtained at the end of each ca. 2000 pulse experimental run.

For electronic spectroscopy of neutral vanadium dioxide, a Nd/YAG pumped dye laser system is used for ionizing and fragmenting clusters. Details of excitation/ionization schemes are presented in next section. The signal from the MCP detector is collected by a boxcar integrator and stored in a computer.

Optimized structures, isomers, ionization energies, relative conformation energies, and vibrational energies for the V_mO_n clusters are calculated at the BPW91/TZVP[23,24] and BPW91/LANL2DZ-D95[23,25] levels employing the Gaussian 98 program[26]. Structures are visualized with the MOLKEL program[27].

III.   RESULTS

1.   <u>Mass Spectra of Neutral Vanadium Oxide Clusters</u>.

Figure 1 shows TOF mass spectra of V_mO_n clusters, observed through 118 nm ionization, for different compositions of the O_2/He expansion/reaction gas mixture (0.5 to 4.0% O_2 at 100 psig total pressure). For these spectra the mass peaks have an average width of ca. 8 ns, which corresponds to the time profile of the seeded Nd/YAG laser. This linewidth indicates that the neutral clusters are ionized without fragmentation[19], as will be discussed in the Section IV below. Higher concentrations of O_2 (to 6% O_2) in the expansion/reaction gas do not change the observed cluster distribution. For less than 3% O_2 in the expansion reaction gas, the cluster distribution and species present change, and oxygen deficient vanadium oxide clusters begin to appear in the neutral cluster distribution. Under saturated O_2 growth conditions (> 3% O_2/He), stable clusters of the form $(VO_2)_x(V_2O_5)_y$ are found. At lower O_2 concentrations the observed clusters are kinetically controlled by the growth process dynamics (e.g., diffusion, temperature, …).

The neutral cluster distribution is not constant throughout the gas pulse as can be readily observed in the detailed mass spectra. Larger clusters appear at the ionization region of the TOF mass spectrometer at later times in the pulse because 1. they take longer to grow in the

reaction zone (plasma plus O_2) of the nozzle, and 2.   they are more difficult to accelerate to

the He beam velocity ($\propto kT$) due to their increased inertia ("velocity slip").[19,28]   These trends

appear applicable even for kinetically controlled growth conditions (0.5% O_2/He mixtures); at

early times in the expansion V_3O_4 is most intense for the V_3O_x series, and at later times V_3O_7

becomes more intense.   For saturated O_2 growth conditions these trends give way simply to

observation of larger clusters, in general, as found for the series V_2O_5, V_3O_7, V_4O_9, V_5O_{12},

V_6O_{14}, and V_7O_{17}.   Clusters V_8O_{19} and V_9O_{20} have also been observed.

Since 118 nm light is generated by tripling 355 nm light, residual 355 nm light (although

defocused to ca. 8 mm) also appears at the ionization region of the TOF mass spectrometer and

can thereby cause some neutral cluster ionization/fragmentation through multiphoton processes.

Figure 2 presents this effect.   Note that the broad VO feature is due almost entirely to 355 nm

larger cluster ionization/fragmentation, while the sharp (~8 ns) VO_2 feature is due solely to 118

nm single photon ionization.   Figure 3 presents mass spectra for larger clusters ionized by 118

nm and 355 nm light.   Spectra (a) and (b) are obtained under the same conditions except that

the 355 nm tripling cell has been evacuated for spectrum (b).   This shows that spectrum (a)

(except for VO^+) is due solely to 118 nm light ionization and that the linewidths (8 ns) for the

features with masses greater than VO^+ imply that no fragmentation has occurred in the

ionization process (for the time range ~1 ns $\leq$ t $\leq$ 10 μs).[19]   The V_2O_5 feature has been

maximized by laser timing and TOF deflection plates.   Fragmented species from 355 nm

multiphoton ionization in spectra (a) and (b) are discriminated against , except for V^+ and VO^+

signals, by maximizing the 118 nm signal and minimizing the 355 nm signal.   The spectrum of

Figure 3c is obtained by maximizing the timing for detection of observed fragmented clusters

seen in the spectrum.   The features of spectrum (c) have linewidths ca. 90 ns.   Note that the

stable, most intense neutral clusters under O_2 saturated growth conditions as given in the figure,

are of the form $(VO_2)_x(V_2O_5)_y$.

The TOF mass spectra of neutral clusters ionized by 193 nm light is presented in Figure 4.   These spectra are obtained under exactly the same experimental conditions as those in Figure 1 except for the ionization laser wavelength.   The mass spectra of V_mO_n clusters reported in ref. 16 correspond to spectra (c), (d), and (e) of Figure 4.   As the O_2 concentration in the expansion gas changes from 0.5% to 3%, the clusters observed are more oxygen rich, as shown for V_2O_n, V_3O_n, V_4O_n, V_5O_n, and V_6O_n clusters.   Nonetheless, the species observed with 118 nm ionization $[(VO_2)_x(V_2O_5)_y]$ under O_2 saturated growth conditions are not observed with 193 nm multiphoton ionization due to fragmentation of the neutral clusters in the ionization process while the 15 ns ArF excimer laser pulse is on.   In all instances the 193 nm detected clusters are more oxygen deficient (due to loss of oxygen atoms in the multiphoton ionization process)   than are those detected with 118 nm single photon ionization.   Note, too, that the mass features in Figure 4 are much broader than are those in Figure 1.   Moreover, this linewidth difference increases for higher concentrations of O_2 in the expansion.

2.   DFT Calculation for Neutral Vanadium Oxide Clusters

As emphasized above, the 118 nm ionization TOF mass spectra of V_mO_n clusters reveal the true stable, neutral vanadium oxide cluster distributions for the given specific growth conditions appropriate for the chosen synthesis conditions of oxygen concentration, timing, backing pressure, etc.   In order to obtain some insight into the structure, energetics, fragmentation, ionization energy, vibrations, and stability of these species, we have employed DFT calculations at the highest levels available to us to address these cluster properties.

The present DFT calculations are performed at the BPW91/TZVP[23,24] and PBW91/LANL2DZ/D95[23,25] levels.   The LANL2DZ/D95 basis sets[25] are, respectively, an effective core potential set for vanadium and a D95 set for oxygen.   We are presently calculating the properties of all species observed for neutral V_mO_n clusters with $m \leq 5$ and

studying their reactions with SO_2, but in this report we will only present data for the O_2

saturated growth, stable, neutral clusters V_2O_4, V_2O_5, V_3O_7, and V_4O_9.

Figure 5 presents optimized structures of the neutral cluster V_2O_4 at the BPW91/TZVP

level.   The energy difference between the cis- and trans-ring structures is small and these two

isomers can change relative energy positions depending on the applied calculational level

(functional, basis set, etc).[3a,d]   The present calculations show that the non-planar (30°), cis-ring

structure is more stable than the nearly planar trans-ring structure by roughly 8 kcal/mol.

Almost surely both structures are present under our experimental conditions.   (VO_2 is

determined to have a vibrational temperature of 700 K = 487 cm^{-1} = 1.4 kcal/mol; ~50% of the

V_2O_4 species could have the high energy isomer structure at this temperature.)   The linear

structure at about 60 kcal/mol higher in energy is probably not present in the beam and will cool

to one of the lower energy geometries if generated in the O_2/metal plasma reaction in the

ablation nozzle.

Optimized structures for the V_2O_5 neutral clusters are given in Figure 6.   We have, as a

test, calculated these structures at the BPW91/TZVP and BPW91/LANL2DZ/D95 levels and

the structure relative energies are presented in Table I for V_2O_5.   Figure 6 shows the relative

energies of the structures for the $^1A'$ and $^3A'$ energy levels of V_2O_5.   Both ring I and linear

structures could be co-existing isomers for our experimental conditions but most likely the ring

I structure is dominant for this ca. 15 kcal/mol energy difference between the two isomers.

These calculations predict a $\tilde{a}^3A' \longleftarrow \tilde{X}^1A'$ electronic transition for these structures at 10,500

cm^{-1} (ring I) and 16,485 cm^{-1} (linear).   We are presently searching for these transitions.

Calculations for the structure and relative energies of neutral V_3O_7 species are presented

in Figure 7 at the BPW91/TZVP level.   Table 2 shows a comparison between the

BPW91/TZVP and /LANL2DZ/D95 levels for this cluster isomer set for the two lowest energy

isomers (I and II of Figure 7).   The agreement between the TZVP and effective core potential

basis set structures and energies seems quite reasonable. $\widetilde{B} \longleftarrow \widetilde{X}$ Note that for the V_3O_7

neutral cluster the lowest energy isomer has a three-dimensional (double ring) structure.   Both

structures I and II can be present in the beam.   We expect that the higher energy isomers will

probably relax to one of these two lower energy isomers in the cooling process.

Optimized structures and relative energies for the V_4O_9 neutral species are given in

Figure 8.   A number of these structures are now three dimensional in nature.   Isomer

structures I, II, III may well be present in the expansion, while the others are probably

depopulated in the cooling process.   DFT results for V_2O_5 and V_3O_7 suggest that the

BPW91/LANL2DZ calculational level gives reliable high level results for structures and

relative isomer energies.

Verticle and adiabatic ionization energies for clusters VO, VO_2, VO_3, VO_4, V_2O_3, V_2O_4,

V_2O_5, and V_2O_6 are calculated and presented in Table 3.   These values ± 0.5 eV, serve as a

rough guide for an estimate of which species should be stable upon 10.5 eV ionization, and also

which species should be possible to ionize with 10.5 eV ionization.   Highly oxidized VO_3 and

VO_4 may not be accessible for ionization under our experimental conditions by a single photon

process.   Note that the TZVP basis set values of ionization energies are about 0.3 eV lower

than those for the LANL2DZ basis set.

3.   <u>Electronic Spetroscopy for VO$_2$ ($\widetilde{B}\ ^2B_2 \longleftarrow \widetilde{X}\ ^2A_1$).</u>

The two detection techniques for observing the mass resolved excitation spectrum of a

given cluster are presented in Figure 9.   One can observe the changes in the mass spectral peak

intensity for a fragment of the cluster created as the parent cluster absorbs energy from a tunable

laser (Scheme I of Figure 9) or one can observe a change in the parent mass feature intensity

itself created by fragmentation due to tunable laser light absorption (Scheme II of Figure 9).

The spectrum of the $\widetilde{B}\longleftarrow\widetilde{X}$ transition of VO_2 can be detected by both methods. Figure 10

presents the overall spectrum for the VO_2 transition detected at the VO^+ mass channel, as

measured by Scheme I, depicted in Fig. 9. VO^+ signal changes are obtained by scanning the dye laser wavelength.   If the dye laser wavelength is resonant with an electronic transition of a cluster, a VO^+ photo-fragmented ion is generated and is observed as the enhanced signal of VO^+. One cannot easily assign, however, to which cluster this observed electronic transition belongs due to the coexistence of various clusters in cluster beam.

Scheme II in Fig. 9 illustrates the excitation scheme for mass selective spectroscopy based on 118 nm single photon ionization.   As described above, 118 nm single photon ionization does not cause cluster fragmentation for metal oxide clusters.   If a wavelength resonant with an electronic transition of the probed cluster causes cluster fragmentation more efficiently than a nonresonant one, a mass selective electronic spectrum for the cluster is observed as a decrease of the probed 118 nm single photon ionization signal.   If clusters fragment into the monitored mass channel, the fragmentation component would appear as an enhancement of the signal probed.   The scanned (spectroscopy) laser must be introduced at the same time as, or earlier than, the 118 nm ionization (probe) laser.

Figure 11 shows the TOF mass spectra observed by (a) 118 and 355 nm, (b) 118, 355, and 608.969 nm (16421.2 cm^{-1}), and (c) 608.969 nm ionization in the VO_x mass region. Spectra (b) and (c) are observed by the schemes corresponded to the Schemes II and I in Fig. 9, respectively.   In spectrum (b), the 608.969 nm wavelength is the observed resonant energy of an electronic transition shown in Fig. 9 (0^0_0).   As seen in spectrum 11 (b), the 608.969 nm laser causes two changes in the mass spectrum: appearance of a new VO^+ signal, which is generated by the 608.969 nm laser at ca. 0.7 μs earlier than the 355 nm VO^+ generated signal; and a decrease of signal intensity of VO_2^+ signal ionized by the 118 nm laser.   Figure 11 (c) shows the mass spectrum observed by 608.969 nm resonant multiphoton ionization alone. 608.969 nm laser creates only a VO^+ signal.   For this experiment, the energy/pulse (~3 mJ) of the 608.969 nm laser is adjusted so that the VO^+ signal is detected only for the wavelength

resonant with the electronic transition. With high pulse energy (10 mJ) of the dye laser at ca. 609 nm, larger clusters with nonresonant multiphoton ionization/fragmentation are observed.

Figure 12 (a) and (d) show dip spectra of the VO_2^+ signal detected by 118 nm ionization, Fig. 12 (b) and (e) show multiphoton ionization (MPI) spectra detected for VO^+, and Fig. 12 (c) and (f) show simulated spectra for VO_2. Figure 12 (a), (b), and (c) present spectra of the transition origin (0_0^0), and Fig. 12 (d), (e), and (f) present spectra of the ν_1 vibronic transition. Rotational envelope simulation for these transitions is performed with rotational constants obtained at the BPW91/TZVP level DFT calculation for the electronic ground state of neutral VO_2 and VO_2^+ singlet cation: for this approximation, we assume that the geometrical structure of cation is similar to the excited state structure. Note that the rotational envelopes for the two detection methods (Schemes I and II of Figure 9) are slightly different. We attribute this difference to the, in principle, separate paths the VO^+ fragment generation and the VO_2^+ parent take to ionization. The VO_2^+ detected envelope relies mostly on the $\widetilde{B} \longleftarrow \widetilde{X}$ and $I \leftarrow \widetilde{X}$ transitions (Scheme II), while the VO^+ detected envelope depends, in principle, on the multiple transitions for $VO_2 \rightarrow VO^+$ (Scheme I). Neither is exactly like the simulation (Figure 12f) because of the simulation assumptions and approximations.

The best fit is for a rotational temperature T_{rot} of about 50 ($\pm$5) K. The dip spectra of VO_2^+ are observed by Scheme II in Fig. 11. The MPI spectra for VO^+ in Figure 12 are expanded spectra of Fig. 10 observed by Scheme I. The dip spectra of VO_2^+ correspond to MPI spectra for VO^+. Laser light at the observed resonant wavelength decreases the population of VO_2 by resonant multiphoton ionization/fragmentation. Therefore, the observed transitions are assigned to originate with the VO_2 cluster. Table 4 gives the observed vibronic transitions for VO_2 and their assignments. The details of the assignments are discussed in the next section.

The intensity ratio for the 1_1^0 and 1_0^1 transitions yields a vibrational temperature T_{vib} of about 700 ($\pm$50) K. This vibrational temperature is similar to that found for VO[16]. A vibrational temperature could also be extracted for the $2_1^0 / 2_0^1$ intensity ratio but the 2_0^1 transition seems to be perturbed and perhaps its intensity is shared between the features at 16710.8 and 16788.7 cm^{-1} (see Table 4).

IV. DISCUSSION

1. Neutral Cluster Distribution

The width of a mass feature in a TOF mass spectrum can reveal information on the nature of the ion (daughter vs. parent) detected. If the cluster does not fragment during the ionization process (parent ion generated), the detected species represents a member of the neutral cluster distribution prior to ionization. Contributions to the ion peak's width include:[19] 1. laser focus size; 2. laser time width; 3. the m/z value of the mass feature; 4. MCP electron transit time (~1.7 ns); and 5. fragmentation time. The contribution to the mass spectral peak width due to spatial distribution of the ionization process increases with increasing mass. 118 nm ionization is by single photon (10.5 eV, ~10^{11} photons/pulse, < 100 μm focus) and the spatial distribution of the laser in the TOF ionization region does not contribute significantly to the peak linewidth for m/z < 500. Thus the averaged linewidth (~ 2000 laser pulses) is found to be the seeded Nd/YAG laser time width, ca. 8.0 ns.

Fragmentation during the ionization process within the time range 1 ns $\lesssim \Delta t \lesssim 10$ μs will affect the observed linewidth of TOF mass features due to the increased spatial distribution of the ions created, and any additional velocity the species might acquire in the fragmentation process. These observations are not restricted to the vanadium oxide system, but are consistent with those made for Zr, Cu, Fe, and Ti oxides.[19] Thus the mass spectral peak linewidth serves as a good indication of the presence or absence of fragmentation in the neutral cluster ionization process.

Using 10.5 eV, single photon ionization for neutral V_mO_n clusters, all clusters, with the possible exception of VO_3 and VO_4 (calculated ionization energy ~ 11.5 eV: See Table 3), will be ionized.   Most V_mO_n neutral clusters have an ionization energy in the range 7 to 10.5 eV.[19,20]   Thus, the cluster excess energy following ionization is ca. 0 to 4 eV.   This is not enough energy to break a V-O bond in such a cluster.[4b]   Even 5 to 6 eV of excess energy in such clusters would not yield fragmentation times (RRKM estimates) within the appropriate time range for observable linewidth effect in large clusters (m, n > 5).   Multiphoton, 355 and 193 nm ionization can of course cause fragmentation within this time range because many photons can be absorbed in the ionization process.[15,18]   Two photon ionization by 355 nm (3.5eV) plus 118 nm photons for clusters with ionization energies larger than 10.5 eV is possible and should also not cause fragmentation of clusters.

With 118 nm ionization, and for saturated oxygen growth conditions ($\geq$ 3% O_2 in the He expansion gas), the observed clusters have the form $(VO_2)_x$ $(V_2O_5)_y$: VO_2 and V_2O_5 are the most intense features detected.   These observations, coupled with the DFT calculated structures presented in Figures 5 through 8, suggest a growth mechanism for V_mO_n neutral clusters. V_2O_4 clusters (Figure 5) can clearly arise from the bonding of two VO_2 (C_{2v}) clusters. V_2O_5 has two structures, ring I and linear (see Figure 6), that probably coexist in the neutral beam.   Both seem to be accessible through the binding of VO_2 and VO_3.   The most stable V_3O_7 structures (I and II of Figure 7) can be formed from the two low energy V_2O_5 structures (Figure 6) by the addition of VO_2 clusters without large displacement of the atoms.   In like manner, V_4O_9 (Figure 8) structures I, II, III can be generated from structure I of V_3O_7 plus VO_2 with only one V-O bond cleavage. V_4O_9 structures I, II, III can also be formed from linear V_2O_5 (Figure 6 II) and two VO_2 species without bond cleavage.   These syntheses probably take place in the ablation plasma/O_2 gas mixing region of the nozzle at temperatures possibly as high as 3000 to 5000 K.

2.   Multiphoton Cluster Fragmentation

From a comparison of Figures 1, 3, 4 one notes that more oxygen poor cluster ions are observed by 193 and 355 nm than by 118 nm ionization.   The linewidths of observed mass peaks for 193 and 355 nm ionization are broader (up to a factor of 10) than those observed for 118 nm ionization especially at higher oxygen concentrations in the expansion/reaction gas. This means that fragmentation has occurred within 1 ns to 10 μs following the ionization laser pulse.   Based on the calculations presented in Figures 5-8 and the energies for single V-O bonds in these clusters, one can suggest that cluster multiphoton fragmentation occurs through loss of oxygen atoms and not V_mO_n units, for laser intensities less than 10^9 W/cm^2 (1 mJ/10 ns pulse, focused to ca. 0.1 mm diameter spot).

Refs. 16 and 18 apply a covariance mapping analysis to learn about cluster growth and fragmentation pathways for different metal oxides, including vanadium oxide, employing 193 nm ionization.   They correctly concluded that, for the vanadium oxide system, the cluster ions observed by 193 nm ionization are related by a growth process.   They further suggested, therefore, that these ions represented the neutral cluster V_mO_n distribution because no true parent ions remain in the mass spectrum.   In the absence of fragmentation, employing 118 nm ionization, the neutral cluster distribution can be identified.   Covariance mapping distinguishes growth and fragmentation relations between cluster species, but if only one or the other pathway is represented by the observed mass features, distinction between the two pathways can be difficult.

3.   Electronic Transition of VO_2

The observed transitions shown in Table 4 and Fig. 10 are assigned to VO_2 as mentioned in the previous section.   Wu et al.[11b] report photoelectron spectra of VO_2 consisting of an unresolved broad feature at ~16410 cm^{-1}.   They assign this feature to the $\tilde{B}$ state of VO_2. Our observed transitions correspond to the energy of the B state feature of their photoelectron

spectrum of VO_2^-.   Knight et al.[21b] report an ab initio calculation of VO_2 in conjunction with an ESR study.   According to their MRSDCI (multireference singles and doubles configuration interaction) calculation with ROHF orbitals, the electronic excited states $^2A_2$ and $^2B_2$ have higher energy by about 2.0 and 3.0 eV, respectively, than the electronic ground state $^2A_1$.

As shown in Fig. 12, rotational simulation of a c-type transition reproduces observed features 0_0^0 and 1_0^1.   Additionally, all the intense transitions for VO_2 listed in Table 4 (marked with "a") that can be observed to decrease the 118 nm generated VO_2^+ signal within the Scheme II detection method of Figure 9 also have the c-type rotational structure of VO_2. VO_2 has the C_{2v} structure and three normal modes ν_1 (symmetric stretch), ν_2 (bend), and ν_3 (antisymmetric stretch), which belong to a_1, a_1, and b_1 symmetry, respectively.   The c-type rovibronic structure means that observed vibronic features belong to symmetry B_2.   Therefore, we can expect that the electronic excited state has A_2 or B_2 symmetry.

If the electronic transition is $\widetilde{B}^2A_2 \leftarrow \widetilde{X}^2A_1$, one can expect to observe vibronic transitions involving ν_3 only ($\Delta v = \pm 1, \pm 3, \ldots$); however, the observed spectrum has the structure of an allowed 0_0^0 transition plus ν_1, ν_2 vibronic hot and cold bands.   These all belong to an electronic transition of VO_2 and all have c-type rotational contours.   Therefore, we assign the observed electronic transition of VO_2 as $\widetilde{B}^2B_2 \leftarrow \widetilde{X}^2A_1$, assigned as shown in Table 4.

Table 5 summarizes the vibrational energies for VO_2 in the $\widetilde{B}^2B_2$ and $\widetilde{X}^2A_1$ states. ν_3 vibrational energy is not obtained experimentally due to low or zero intensity for b_1 modes for a C_{2v} molecule in the $\widetilde{B}^2B_2 \leftarrow \widetilde{X}^2A_1$ transition.

The observed transition is assigned to VO_2 because the ion dip spectrum (Scheme II of Figure 9) is observed on the 118 nm ion signal for VO_2.   This spectroscopic technique also proves that neutral VO_2 is ionized to VO_2^+ by 118 nm single photon ionization without fragmentation.

V.   CONCLUSIONS

In this study, single photon, 10.5 eV ionization has been employed to determine the distribution of neutral vanadium oxide clusters generated in the gas phase by laser ablation of the metal into mixtures of oxygen and helium.   DFT calculations of neutral cluster structures and ionization energies suggest that the observed cluster ions generated, employing 10.5 eV ionization, are indeed representative of the neutral cluster distribution prior to ionization.   Of the clusters calculated, only VO_3 and VO_4 have higher ionization energies (11.5 eV); the VO_3 cluster is observed only for conditions such that 355 plus 118 nm two photon ionization is possible.   These conclusions are supported by RRKM calculations, linewidth data, and available ionization energy data.   Neutral clusters for saturated oxygen growth conditions are found to be of the form $(VO_2)_x(V_2O_5)_y$.   Cluster growth prior to ionization is suggested to be through VO_2 or V_2O_5 addition to $(VO_2)_a$ and $(V_2O_5)_b$ species, such that the stable neutrals (saturated oxygen growth) are VO_2, V_2O_4, V_2O_5, V_3O_7, V_4O_9, V_5O_{12}, V_6O_{14}, V_7O_{17}, ….

Cluster fragmentation due to multiphoton absorption during the ionization processes associated with relatively low laser energy/pulse 193 and 355 nm ionization is suggested to occur by loss of oxygen atoms singly bonded to vanadium atoms in the cluster, based on DFT structure calculations and energetic considerations.

Observation of the $\widetilde{B}^2B_2 \leftarrow \widetilde{X}^2A_1$ transition for VO_2 at 16,421.2 cm^{-1} (0^0_0) yields rotational and vibrational temperature information for small clusters: $T_{rot} \sim 50$ K and $T_{vib} \sim 700$ K.   This spectrum is uniquely assigned to the VO_2 cluster through ion dip spectroscopy employing 118 nm single photon ionization for the clusters.   These results further support the contention that 118 nm radiation at ca. 1 μJ/pulse energy does not fragment the clusters.

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