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# Formation and distribution of neutral vanadium, niobium, and tantalum oxide clusters: Single photon ionization at 26.5 eV

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Neutral vanadium, niobium, and tantalum oxide clusters are studied by single photon ionization employing a 26.5 eV/photon soft x-ray laser. During the ionization process the metal oxide clusters are almost free of fragmentation. The most stable neutral clusters of vanadium, niobium, and tantalum oxides are of the general form $(MO_2)_{0,1}(M_2O_5)_y$. $M_2O_5$ is identified as a basic building unit for these three neutral metal oxide species. Each cluster family ($M_m$, $m=1,\ldots,9$) displays at least one oxygen deficient and/or oxygen rich cluster stoichiometry in addition to the above most stable species. For tantalum and niobium families with even $m$, oxygen deficient clusters have the general formula $(MO_2)_2(M_2O_5)_y$. For vanadium oxide clusters, oxygen deficient clusters are detected for all cluster families $V_m$ ($m=1,\ldots,9$), with stable structures $(VO_2)_x(V_2O_5)_y$. Oxygen rich metal oxide clusters with high ionization energies (IE$>$10.5 eV, 118 nm photon) are detected with general formulas expressed as $(MO_2)_2\ (M_2O_5)_y\ O_{1,2,3}$. Oxygen rich clusters, in general, have up to three attached hydrogen atoms, such as $VO_3H_{1,2}$, $V_2O_5H_{1,2}$, $Nb_2O_5H_{1,2}$, etc. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358980]

## I. INTRODUCTION

Transition metals, as well as their oxides, carbides, nitrides, and sulfides, are unique in their abilities to catalyze chemical reactions, primarily due to their multiplicity of low energy surface electronic states, which can readily donate and/or accept electrons in the process of making or breaking bonds at a surface.[1] Transition metal oxides are employed extensively as catalysts in the chemical industry, for example, vanadium oxide catalysts are used in the generation of sulfuric acid.[2] The microscopic properties of specific local catalytic sites and the mechanisms for catalytic activity of these metal oxide catalysts are still not elucidated. Catalytic properties of a material (activity, selectivity, and stability) are, in general, determined by chemical (electronic) properties of surface atoms/molecules.[3,4] Metal/metal oxide clusters generated in the gas phase are considered to be an ideal model system for the local surface of the condensed/surface phase because of their relatively well defined structures, size dependent properties, and their relative ease of accessibility by theory. To explore the reactivity and behavior of metal and metal oxide clusters, one must first understand their neutral cluster distributions, growth patterns and pathways, structures, and electronic properties.

Neutral metal oxide clusters tend to have high ionization energies ($8 \leqslant \mathrm{IE} \leqslant 10$ eV or more) especially for oxygen rich clusters for which most of the metal electrons are involved in bonding interactions. Due to this high ionization energy, the clusters require multiphoton absorption in order to be detected by mass spectroscopy techniques. Even multiphoton ionization is typically thought to be more gentle than electron ionization. Multiphoton absorption by clusters is often difficult to control due to the neutral or ionic cluster ability to absorb many photons. Neutral clusters can thereby ionize at high, superexcited, unrelaxed electronic states or by thermionic emission through rapid electronic relaxation and heating of the neutral cluster. In either event cluster fragmentation, and thus loss of neutral cluster distribution information, is

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often the end result.[5,6] On the other hand, single photon near threshold ionization at low laser fluence yields little fragmentation and thus maximum neutral cluster information.[7]

Recently, mass selected metal oxide cations of vanadium, niobium, and tantalum have been studied with regard to their photodissociation properties. In order to determine the most stable cations of metal oxide clusters, selected cluster cations are exposed to 532 and 355 nm laser radiation and undergo multiphoton (resonant) absorption.[8] Cluster cation distributions are similar for these three metal oxides. The most stable cluster cations are of the formulas $MO_2^+$, $M_2O_4^+$, $M_3O_7^+$, $M_4O_9^+$, $M_5O_{12}^+$, $M_6O_{14}^+$, and $M_7O_{17}^+$ [i.e., general $(MO_2)_x(M_2O_5)_y^+$]. Collision induced dissociation of vanadium oxide cluster cations[9(a)] and anions[9(b)] and niobium oxide[10] cations has also been studied. The most stable cluster ions with high dissociation energies are identified as $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_{8,9}^+$, $V_5O_{11,12}^+$, and $V_6O_{13,14}^+$ for the vanadium cluster ion system, and $Nb_3O_7^+$, $Nb_4O_{9,10}^+$, and $Nb_5O_{12}^+$ for the niobium cluster cation system. The distribution of metal oxide ions is somewhat different than that of the neutral clusters, however. Vanadium oxide neutral clusters have been ionized by single photon absorption of near ionization threshold photon energy (10.5 eV, 118 nm).[11] A potential question about this ionization technique for determination of neutral cluster distributions is, of course, whether 10.5 eV is sufficient energy to ionize all, even oxygen rich neutral species. Vacuum ultraviolet (VUV) photoionization at 118 nm has the best chance to ionize clusters without fragmentation and thus to be able to detect the most abundant neutral clusters found in a molecular beam. Employing 118 nm ionization and saturated oxygen growth conditions, the most abundant neutral clusters are assigned to the form $(VO_2)_x(V_2O_5)_y$. Cluster rotational and vibrational temperatures for $VO_2$ are determined to be 50 and 700 K, respectively. Nonetheless, species such as $VO_3$, $VO_4$, and $V_2O_6$ have ionization energies higher than 10.5 eV (Ref. 11) and are not detected in these experiments.

A new tabletop, 26.5 eV/photon, 46.9 nm extreme ultraviolet (EUV), soft x-ray laser is employed in the present study to ensure that all species in the neutral cluster metal and metal oxide distributions are detected. As we will demonstrate, the EUV laser not only ionizes all species in these experiments, but it is a very gentle ionization source that does not fragment, even metastable, slow fragmentation, any of the clusters of interest. In the present experiment, neutral metal oxide clusters of vanadium, niobium, and tantalum are studied by single photon ionization at 26.5 eV. The neutral cluster distributions, generated under saturated oxygen conditions for metal oxide cluster growth, are determined for these three metals. The most stable neutral metal oxide clusters are determined. The structure and formation of these clusters are discussed in detail. Oxygen rich neutral clusters are detected for the first time and are found to have up to three attached hydrogen atoms.

## II. EXPERIMENTAL PROCEDURES

Since the experimental apparatus has been described in detail elsewhere,[12] only a general outline of the experimental scheme will be presented in this report. Briefly, vanadium, niobium, and tantalum oxide neutral clusters are generated in a conventional laser vaporization/supersonic expansion cluster source by laser ablation of vanadium, niobium, or tantalum metal foil into a carrier gas mixed with 5% $O_2$ at 80 psig. Pure metal clusters can also be generated by laser ablation of the metal into a pure He (99.995%) expansion gas. A 532 nm wavelength laser [second harmonic of a Nd/YAG laser (YAG denotes yttrium aluminum garnet), 1064 nm] is employed to ablate the metals at 5–10 mJ/pulse. Ions created in the metal ablation/metal oxide growth process are removed from the supersonic expansion by an electric field outside the nozzle in the vacuum system. Neutral clusters pass through a skimmer with a 4 mm aperture into the ionization region of a time of flight mass spectrometer (Wiley-McLaren design, R.M. Jordan Co.). The clusters are ionized by three different nanosecond pulsed lasers: 193 nm (ArF), 118 nm (ninth harmonic of a seeded Nd/YAG, 1064 nm laser), and a 46.9 nm EUV soft x-ray laser.

The x-ray laser (26.5 eV/photon energy) emits pulses of about 1 ns duration with an energy/pulse of 10 $\mu$J at a repetition rate of up to 12 Hz. A time of flight (linear/reflectron) mass spectrometer (TOFMS) is employed for mass analyzer.[12] A pair of mirrors placed in a *Z*-fold configuration just before the ionization region of the TOFMS provides alignment and focusing capabilities for the laser with respect to the molecular cluster beam at the focus of the TOFMS in the ionization region. The *Z*-fold mirror system has a transmissivity of about 10%. Since the 26.5 eV photons from the EUV laser are able to ionize the He carrier gas employed in the expansion, the microchannel plate (MCP) ion detector voltage is gated to reduce the gain of the MCP when $He^+$ arrives at the mass detector in order to prevent detector circuit overload and saturation.

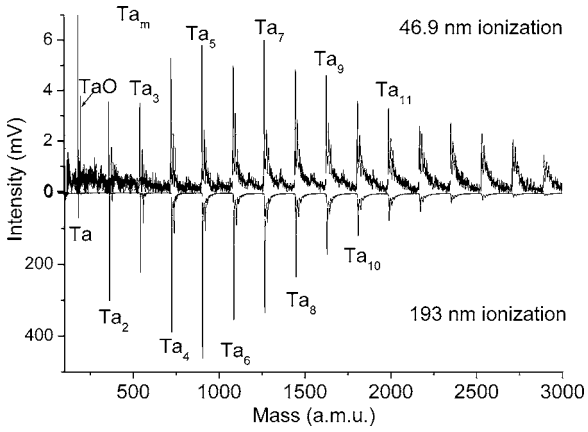



FIG. 1. Linear TOF mass spectrum of pure tantalum metal cluster ionized by 26.5 eV laser (upper) and 193 nm laser (lower), respectively. Sharp features to the high mass side of each $Ta_m$ peak are due to $Ta_mO_x$ and $Ta_mC_y$ clusters generated by impurities in the gas, vacuum, and metal surfaces and bulk. Exactly the same spectra arise for reflectron mode operation of the TOFMS. Metastable (slow) fragmentation does not occur from either 193 or 46.9 nm single photon ionization.

## III. RESULTS

Figure 1 displays a linear TOF mass spectrum of tantalum metal clusters ($Ta_m$) generated with a pure He expan-

sion. These spectra are identical to those obtained with the TOFMS operated in reflectron mode. In the bottom spectrum, the neutral clusters are ionized through an unfocused 193 nm laser beam at a fluence of 100 $\mu J/cm^2$; the possibility of multiphoton processes from these photons is quite small. The IE of Ta atom is 7.9 eV.[13] The vertical IE (VIE) for $Ta_m$ clusters decreases with increasing cluster size and is measured approximately 5–6 eV for different cluster sizes $m=3-10$.[14] Thus the single 193 nm (6.4 eV) photon has sufficient energy to ionize neutral $Ta_m$ clusters but not enough energy to ionize the Ta atom in its ground electronic state. Thus $Ta_m$ $(m \geqslant 2)$ cluster ions are observed in this experiment, and the small $Ta^+$ signal is detected due to either hot Ta atoms or a weak multiphoton component to the ionization. The upper spectrum is obtained for the same $Ta_m$ sample employing the 26.5 eV/photon soft x-ray laser for ionization. The cluster distribution obtained through the two different single photon ionization sources is nearly identical as shown in Fig. 1. The minor differences in peak intensities for $Ta_m$ $m>2$ are probably due to small ionization cross section differences at the different laser wavelengths. Clearly Ta and TaO species have low cross sections for ionization at 193 nm but considerable cross sections at 46.9 nm. The pulse energy at 46.9 nm is below 1 $\mu$J, and thus for both lasers, only the single photon ionization needs to be considered. The bond energy of $Ta_m$ is measured to be approximately 5–7 eV,[14–16] and a single photon of 6.4 eV is not energetic enough to both ionize and fragment a $Ta_m$ cluster. In other words, the cluster ion distribution $Ta_n^+$ $n>2$ reflects quite accurately (cross section issues aside) the neutral cluster distribution and clearly shows the 26.5 eV distribution. The 26.5 eV distribution of $Ta_n^+$ $n>1$ reflects the total distribution of species in the supersonic expansion beam (again, cross section issues aside). Since both distributions are so similar, cross section differences as a function of wavelength must not be terribly important here. The photoelectron must remove nearly 20 eV of excess energy as it exits the cluster to avoid fragmentation of the cluster through 26.5 eV ionization. Recall that even metastable fragmentation is eliminated by the reflectron spectrum (not shown). Study of the photoelectron spectra at 26.5 eV photon energy for these metal clusters would certainly prove interesting and informative. Thus 26.5 eV causes little or no fragmentation in ionizing transition metal clusters, in general.

Figure 2 shows the TOF mass spectra of $Ta_mO_n$ clusters generated with 5% $O_2$/He expansion using three different wavelengths for ionization. In Fig. 2(a), only $Ta^+$, $TaO^+$, and $TaO_2^+$ are observed for ionization with 193 nm laser radiation. The VIEs of TaO and $TaO_2$ are about 8 and 9 eV,[17,18] respectively. These ion signals must be generated through multiphoton ionization. The absence of larger clusters in this mass spectrum implies a great deal of fragmentation during the multiphoton ionization process(es). The large intensities in the $TaO^+$ and $TaO_2^+$ mass channels must come from the fragmentation of large clusters. The mechanism for these fragmentations will be described in the next section. The power of the 193 nm light can be decreased in order to reduce fragmentation by the absorption of too many photons, but larger clusters are still not observed.

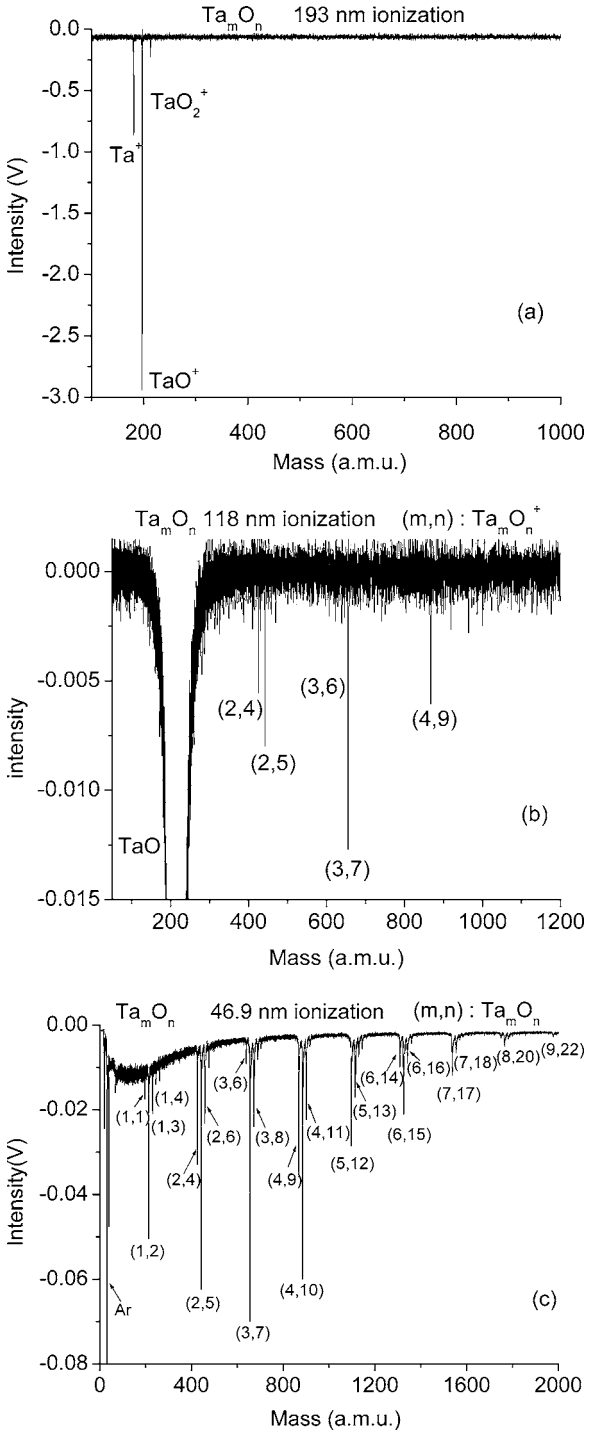



FIG. 2. TOF mass spectra of tantalum oxide clusters ionized at three different wavelengths: (a) multiphoton ionization at 193 nm, (b) near threshold single photon ionization at 118 nm, and (c) single photon ionization at 46.9 nm.

Figure 2(b) shows the mass spectrum observed, under the same experimental conditions, upon changing the ionization source to 118 nm light. A number of larger cluster ions are observed through this ionization. Note that no oxygen rich clusters (e.g., $Ta_2O_6$, $Ta_3O_8$, $Ta_4O_{11}$, etc.) are observed, however. The 10.5 eV photon energy is sufficient to ionize most $Ta_mO_n$ clusters in the beam. The predominant detected cluster ions are $TaO_2$, $Ta_2O_{4,5}$, $Ta_3O_{6,7}$, and $Ta_4O_9$ with the general formula $(TaO_2)_x$ $(Ta_2O_5)_y$. Since 118 nm light is

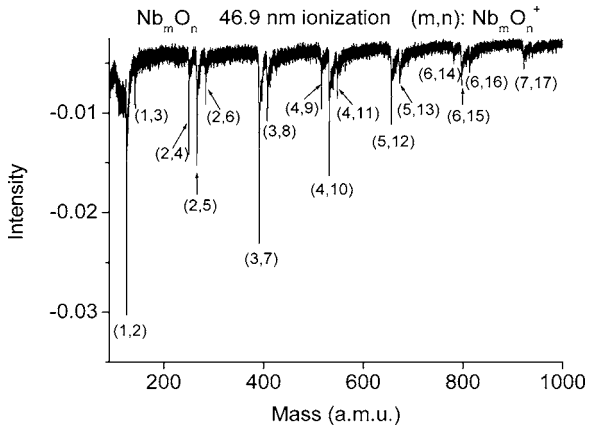



FIG. 3. TOF mass spectrum of niobium oxide clusters ionized by 26.5 eV soft x-ray laser photons. The sample is generated by laser ablation of Nb metal into a 5% $O_2$/He gas mixture and 80 psi backing pressure.

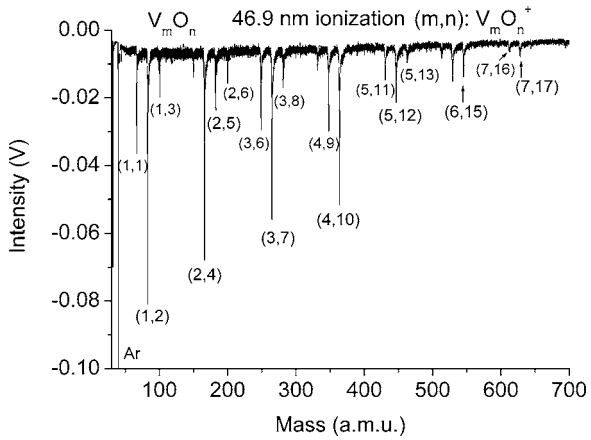



FIG. 4. TOF mass spectrum of vanadium oxide clusters ionized by 26.5 eV soft x-ray laser photons. The sample is generated by laser ablation of V metal into a 5% $O_2$/He gas mixture and 80 psi backing pressure.

generated by tripling 355 nm, even though the optical arrangement reduces the fluence of 355 nm light at the ionization point (focus of 118 nm light[7]) to less than the 118 nm fluence (approximately $10^{-6}$ of its original value), residual 355 nm also appears at the ionization/focal point of the TOFMS. Thus 355+118 nm multiphoton (perhaps resonant) excitation, ionization, and fragmentation can occur for the $Ta_mO_n$ neutral clusters: this process is probably responsible for the broad intense signal in the $TaO^+$ mass channel [see Fig. 2(b)].

Figure 2(c) shows a mass spectrum of $Ta_mO_n$ clusters obtained with 26.5 eV (46.9 nm) single photon ionization from the soft x-ray EUV laser. As shown, cluster ion signals are generated for species with up to nine Ta atoms, $TaO^+$ and $Ta^+$ display very small signals, and the observed features are quite sharp (approximately 10–20 ns). Compared with the 118 nm ionization spectrum [Fig. 2(b)], more stable clusters are observed, especially oxygen rich clusters such as $TaO_3$, $Ta_2O_6$, $Ta_3O_8$, $Ta_4O_{11}$, etc. with 26.5 eV ionization. Even highly oxygen rich clusters such as $TaO_{4,5}$ are detected in the low mass region. Note that $Ta^+$ is not observed and that only very small $TaO^+$ signal is observed.

The differences between $Ta_mO_n$ mass spectra obtained with the three laser wavelengths (see Fig. 2) in these studies can be associated with three different contributing factors. First, most of the Ta atoms generated by laser ablation of the metal foil react with $O_2$ in the nozzle to form $Ta_mO_n$ clusters. Thus the large $Ta^+$ and $TaO^+$ signals arise in the 193 and 118/355 nm generated mass spectra are generated through fragmentation of large clusters due to multiphoton ionization processes. Second, the photoionization cross section of the metal at 26.5 eV may just be much smaller than that at 193 nm. One can see from Fig. 1 that this is at least partially correct. The signal intensity for $Ta_m^+$ at 26.5 eV ionization is 3–10 mV (Fig. 1), while the signal intensity for $Ta_mO_n^+$ at 26.5 eV ionization is 20–80 mV (Fig. 2). Third, fragmentation of large clusters does not occur for 26.5 eV ionization because of its single photon nature, as the exiting electron must remove most, if not all, of the cluster excess energy over the VIE (see Sec. IV below). Thus fragmentation of larger clusters does not contribute significantly to the small $Ta^+$ and $TaO^+$ signals to the presence of these neutrals in the expansion. These very small species have grown into the larger clusters and their presence in the beam is greatly reduced.

The TOF mass spectrum of niobium oxide clusters ($Nb_mO_n^+$), ionized by 26.5 eV soft x-ray laser photons, is presented in Fig. 3. The predominant ion signals are assigned as $NbO_2$, $Nb_2O_5$, $Nb_3O_7$, etc. These stoichiometries are similar to those found for the $Ta_mO_n$ system. The distribution of 26.5 eV ionized vanadium oxide clusters is shown in Fig. 4. The predominant $V_mO_n$ features in this spectrum are in agreement with those for niobium and tantalum oxide clusters with the exception of $V_2O_4^+$ which is much more intense relative to the other spectral features than that found for $Nb_2O_4^+$ and $Ta_2O_4^+$. Also the vanadium oxide spectrum shows some new stoichiometric features compared to niobium oxide and tantalum oxide spectra of Figs. 3 and 2(c), respectively: these new peaks include $V_5O_{11}$ and $V_7O_{16}$. The formation mechanism of the neutral vanadium, niobium, and tantalum oxide clusters will be discussed in the next section.

Figure 5 displays the mass spectrum of $V_mO_n$ clusters obtained through 193 nm (multiphoton) ionization. In this mass spectrum oxygen deficient cluster ions are most intense

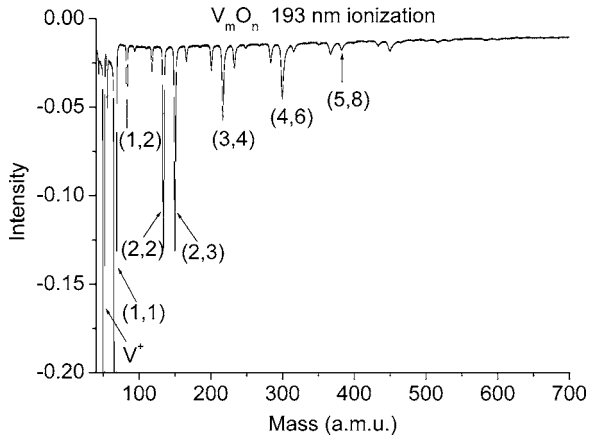



FIG. 5. TOF mass spectrum of vanadium oxide clusters ionized by 193 nm laser photons. The sample conditions are the same as those employed for the spectrum shown in Fig. 4.

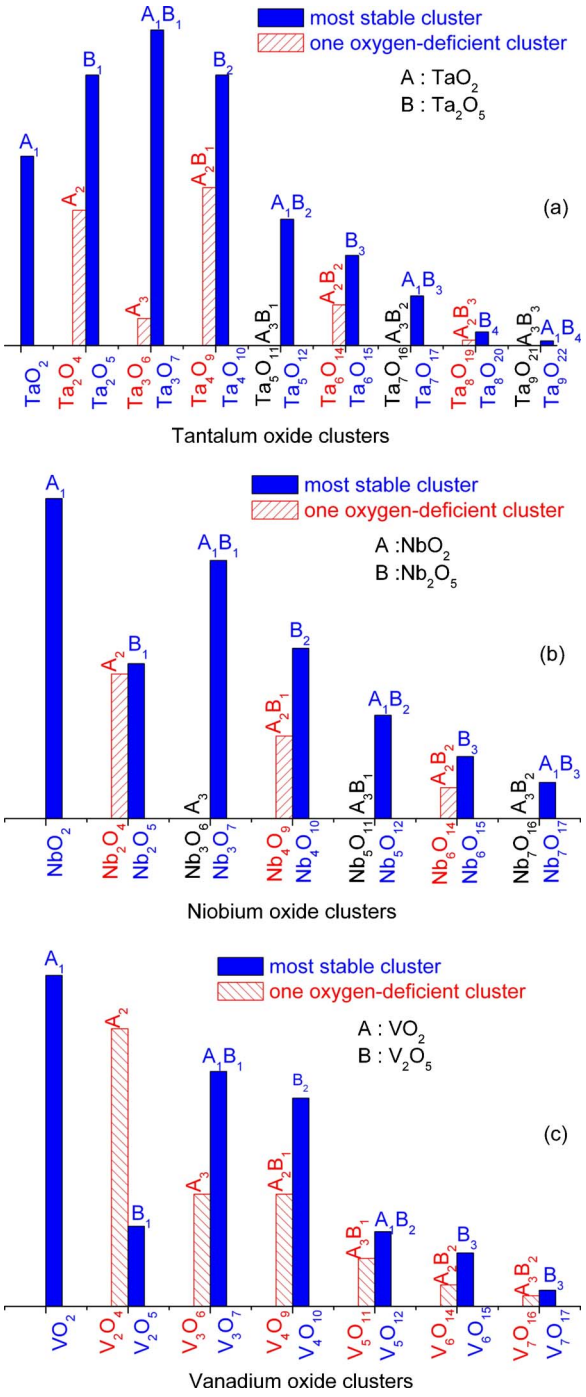



FIG. 6. (Color online) Distributions of the most stable and oxygen-deficient clusters for (a) tantalum, (b) niobium, and (c) vanadium, respectively. $MO_2$ and $M_2O_5$ are used as basic units to build the oxide clusters.

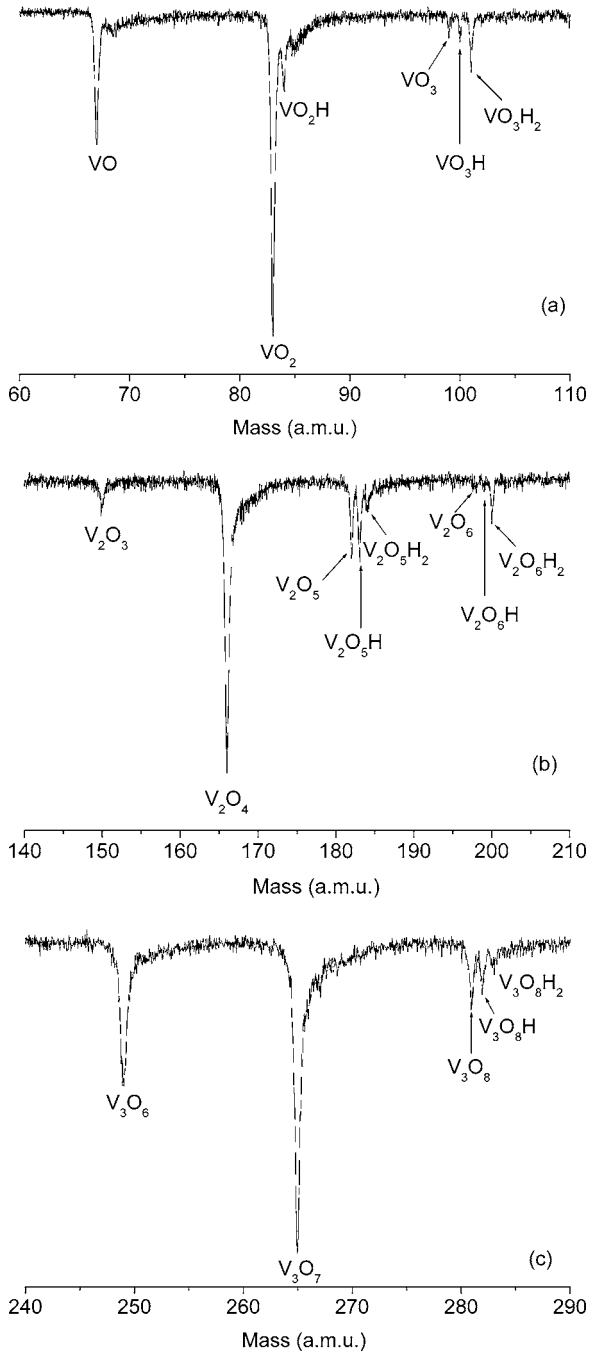



FIG. 7. Expanded portions of the mass spectra of Fig. 4 for the following regions: (a) VO, $VO_2$, and $VO_3$; (b) $V_2O_3$, $V_2O_4$, $V_2O_5$, and $V_2O_6$; and (c) $V_3O_6$, $V_3O_7$, and $V_3O_8$. One or two hydrogen atoms are attached to oxygen rich vanadium oxide clusters. Similar behavior also occurs for niobium and tantalum oxide clusters.

(e.g., $V_3O_4$, $V_4O_5$, $V_5O_7$, etc.). The signal pulses are also very broad (approximately 100 ns). This observation is in agreement with our previous report.[11] Additionally, intense features at mass $V^+$ and $VO^+$ are observed due to fragmentation of larger clusters; however, no $V^+$ and little $VO^+$ signals are observed for 26.5 eV ionization (Fig. 4), as no fragmentation occurs for this ionization mode.

The distribution of metal oxide clusters with the most stable (abundant) stoichiometries for the three systems are given in Fig. 6: these are plotted based on the data of Figs. 2(c), 3, and 4. Note that $MO_2$ and $M_2O_5$ can be used as basic building blocks for the three metal oxide clusters. Systematics for oxygen deficient cluster growth are discussed below.

At high dispersion for 26.5 eV single photon generated mass spectra, one observes that a number of $M_mO_n$ clusters appear to have associated peaks of 1 and 2 amu higher mass, as shown in Fig. 7. These metals V, Nb, and Ta are all single isotope species. The extra features typically appear for oxygen rich or oxygen sufficient clusters. This is the first time such features have been observed because all clusters in the beam are ionized at 26.5 eV photon energy and little or no cluster fragmentation occurs upon ionization; apparently

10.5 eV photons cannot or do not ionize such species. The source of hydrogen in the clusters is not clear, but $H_2O$, some hydrocarbon, $H_2$ absorbed in the metal, or surface OH may all be possible contenders. These species will be discussed in the next section.

## IV. DISCUSSION

### A. Fragmentation mechanism for $M_mO_n$ clusters ($M$=V, Nb, Ta)

A single photon of 193 nm wavelength does not have enough energy (~6.4 eV) to ionize the metal oxide $M_mO_n$ clusters of interest in this study. At least two photons of 6.4 eV energy are required to ionize TaO (VIE ~8.0 eV) and $TaO_2$ (VIE ~9.0 eV) and other larger clusters. Since intracluster vibrational redistribution (IVR) of energy occurs rapidly in these clusters, a part of the absorbed photon energy before and during ionization is used to heat the clusters. These IVR dynamics lead to the predissociation (fragmentation) of metal oxide clusters. No large $Ta_mO_n$ cluster is detected through 193 nm ionization [Fig. 2(a)]; these clusters are fragmented in the ionization process by multiphoton (more than two) absorption into of $TaO^+$ and $TaO_2^+$. The TOFMS features at $Ta^+$, $TaO^+$ and $TaO_2^+$ are sharp and symmetric implying that a fast predissociation of neutral clusters $Ta_mO_n$ occurs during and/or following the 193 nm laser pulse ($<\sim 1$ ns). Additionally, this predissociation process is rapid and violent enough to dissociate large clusters into small components to form $Ta^+$, $TaO^+$, or $TaO_2^+$ ions only.

In like manner, $Nb_mO_n$ neutrals yield $Nb^+$, $NbO^+$, and $NbO_2^+$ small fragments upon 193 nm multiphoton ionization. Thus similar fragmentation dynamics are appropriate for $Ta_mO_n$ and $Nb_mO_n$ neutral clusters.

The dynamical behavior for vanadium oxide clusters, upon multiphoton ionization by 193 nm photons under the same experimental conditions employed for $Nb_mO_n$ and $Ta_mO_n$, is quite different. As Fig. 5 demonstrates, a number of oxygen deficient vanadium oxide cluster ions, such as $V_2O_3^+$, $V_3O_3^+$, $V_3O_4^+$, $V_4O_6^+$, and $V_5O_8^+$, are detected under 193 nm ionization. The two possible reasons for observation of these oxygen deficient vanadium oxide clusters under these conditions are as follows: (1) direct, single photon ionization from the neutral oxygen deficient clusters present in the supersonic beam, and (2) such clusters are formed from neutral stable clusters $(VO_2)_x(V_2O_5)_y$ by loss of several oxygen and vanadium atoms during the multiphoton ionization process. Reason (1) implies that these oxygen deficient, neutral vanadium oxide clusters $V_2O_2$, $V_3O_3$, $V_3O_4$, $V_4O_6$, and $V_5O_8$ have low (<6.4 eV) VIEs. In the 26.5 eV derived mass spectrum of $V_mO_n$ these oxygen deficient vanadium oxide clusters are not observed. We therefore conclude that through comparison with the other two systems and a knowledge of the VIEs of small clusters, the $V_mO_n$ cluster ions observed by 193 nm ionization arise due to fragmentation of larger stable clusters present in the beam prior to the ionization process. This is in fact what has happened for all three cluster systems during ionization, and different products for $V_mO_n$ vs $Nb_mO_n$ and $Ta_mO_n$ must arise from the details of the number of photons absorbed by the clusters, the cluster densities of states, and the overall cluster system ensuing dynamics.

### B. Distribution of the neutral V, Nb, and Ta oxide clusters

Metal oxide (and metal) clusters are bonded by chemical covalent bonds, and due to unpaired electrons, which typically have a very large number of vibronic states and a very high density of states. This situation enables very rapid radiationless transitions. Multiphoton excitation is thereby quite probable for those systems and can lead to cluster fragmentation and thereby loss of neutral cluster identity based on mass spectral data. Single photon, near threshold ionization is the best approach to the detection and identification of the true neutral cluster distribution. Metal oxide clusters such as $Fe_mO_n$, $Ti_mO_n$, $V_mO_n$, $Cu_mO_n$, etc.,[7,11] have been studied by single photon ionization by 118 nm (10.5 eV) light. The distributions of neutral clusters for these systems have thus been determined; however, some neutral metal oxide clusters (e.g., highly oxidized ones, $VO_3$, etc.) have VIEs >10.5 eV and are thus not detected by this approach.

We have demonstrated in this work (see Fig. 1) and in other reports from our laboratory [$(H_2O)_n$, $(CH_3OH)_n$, $(NH_3)_n$, $(SO_2)_n$, $(CO_2)_n$, metals, etc.[12]] that 26.5 eV single photon ionization can also generate mass spectra that are not overwhelmed by fragmentation, and that can lead to a complete and quite accurate description of the neutral parent cluster distribution in the preionized, supersonic beam. Proof that these mass spectral representations of neutral cluster distributions are accurate comes from a comparison between VUV (118 nm), EUV (46.9 nm), and resonance lamp (Ar, etc.) generated TOFMS.[12] Just how the photoelectron removes the cluster excess energy (possibly approximately 15–20 eV for 26.5 eV ionization) is a topic of some interest which we are addressing through photoelectron spectroscopy to discover the processes and electrons involved in the ionization step. The advantage of 26.5 eV single photoionization over other less energetic single photon photoionization sources is that the soft x-ray EUV photon ionizes everything. Thereby, the spectra of Figs. 1, 2(c), 3, and 4 are an excellent representation of the neutral clusters in the supersonic expansion prior to ionization for the respective system.

One of course must be aware that VIEs are not AIEs, and thus some excess energy will always remain in the newly formed ions and if this is enough to fragment the cluster (e.g., possibly through a reaction, proton transfer[19]) one cannot expect, except through detailed analysis of the mass spectrum,[12] to take the single peak intensities at face value. The distribution of neutral clusters synthesized in a laser ablation source can, in principle, reflect the effects of growth kinetics in addition to thermodynamic stability of clusters. The distribution detected in these experiments tends to a stable relation at the condition of greater than 4% $O_2$ in the expansion gas. The same results are reported for the previous 118 nm ionization experiments.[11] Thus, the results support the conclusion that the neutral cluster distribution observed is not the result of growth kinetics. Additionally, single pho-

ton ionization cross sections could be wavelength dependent, and different ionization photon energies could yield different relative mass spectral intensities. Nonetheless, the data present in Fig. 1 and our previous publications are quite compelling. Moreover, structure calculations for vanadium oxide clusters suggest that $VO_2$, $V_2O_5$, $V_3O_7$, $V_4O_{10}$, $V_5O_{12}$, and $V_6O_{15}$ are the most stable clusters for $V_nO_m$, $n=2-6$ in agreement with the distribution observed with 26.5 eV single photon ionization.

Upon ionization by 26.5 eV EUV light, the most stable neutral clusters are identified as $MO_2$, $M_2O_4/M_2O_5$, $M_3O_7$, $M_4O_{10}$, $M_5O_{12}$, $M_6O_{15}$, $M_7O_{17}$, $M_8O_{20}$, and $M_9O_{22}$ for vanadium, niobium, and tantalum oxide clusters. This determination is based on the above discussed comparisons of differently generated mass spectra.

For $Ta_mO_n$ and $Nb_mO_n$ clusters, the odd families ($M_m$, $m$ is odd) show little or no oxygen deficient cluster concentration, and for even $m$ these species do have oxygen deficient clusters. Here we consider oxygen deficient and oxygen rich clusters as defined with respect to the most stable clusters $(MO_2)_{0,1}(M_2O_5)_y$ based on intensity for 118 and 46.9 nm ionization. Vanadium oxides are apparently more flexible in their stoichiometry as oxygen rich and oxygen poor clusters appear for most cluster families $V_m$.

One set of features for these three metal oxides, ionized by 118 and 46.9 nm radiation, does not fall into the general systematic discussed above: these peaks are for the $M_2$ family of clusters. For $Nb_2O_{4,5}$ and $Ta_2O_{4,5}$ the $M_2O_5$ feature is the most intense (stable) neutral cluster and ion by either 118 or 46.9 nm ionization, while for $V_2O_m$ 118 nm ionization[11] finds $V_2O_5^+$ more intense than $V_2O_4^+$ which is contrary to the 46.9 nm ionization. This difference does not relate to the presence of $M_2O_5H_x$ clusters in the system and is probably most readily associated with the details of wavelength dependent ionization cross sections for $M_2O_4$ and $M_2O_5$ neutral clusters.

### C. Structure and formation of neutral clusters

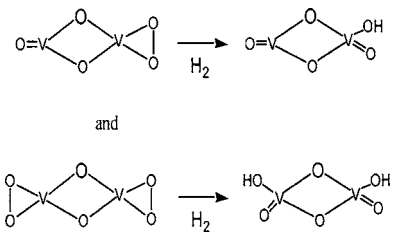
The most common bulk stoichiometry for group V (V, Nb, Ta) transition metal oxides in $M_2O_5$, indicates that the metal has an effective oxidation state of +5 with +4 also a viable state in oxides such as $VO_2$ and $V_2O_4$. $MO_2$ and $M_2O_5$ are thereby reasonable suggestions for the main building blocks for these metal oxide cluster series. As shown in Fig. 6, stoichiometry of the most stable metal oxide clusters (that is, most intense mass spectral features) can be expressed as $(MO_2)_{0,1}(M_2O_5)_y$. One can conclude that a $M_2O_5$ unit is the basic building block for the main cluster family ($M_m$) feature, with only at most one $MO_2$ unit appearing in clusters of the most stable stoichiometry. Based on the premises that 26.5 eV photons do little in the way of cluster fragmentation and that 26.5 eV photons can ionize any species in the expansion, the TOF mass spectra at 26.5 eV ionization represent all clusters and both their neutral and cation populations.

Cluster family structure and stoichiometry can be seen to be systematic for $Nb_mO_n$ and $Ta_mO_n$ clusters. Typically for even $m$, oxygen deficient, oxygen sufficient, and oxygen rich clusters are observed. Thus $M_2O_{4,5,6}$, $M_4O_{9,10,11}$, $M_6O_{14,15,16}$, etc., where $M$=Nb, Ta are observed. On the other hand, for odd $m$ families, oxygen deficient clusters are not observed. The only exception to this general rule is $Ta_3O_6$ which is very weak, as shown in Fig. 2(c). Oxygen deficient clusters can be represented as $(MO_2)_2(M_2O_5)_y$ and the oxygen rich clusters as $(MO_2)_{0,1}(N_2O_5)_yO_{1,2,3}$.

This odd/even family difference found for $Nb/Ta_mO_n$ clusters is not found for $V_mO_n$ clusters. In these species all clusters $V_mO_n$ have oxygen deficient and oxygen rich clusters relative to the most stable one. $V_nO_n$ clusters can be represented as $(MO_2)_x(M_2O_5)_y$ for oxygen deficient and sufficient clusters and for oxygen rich clusters as $(MO_2)_x(M_2O_5)_yO$, as appropriate. Structure calculations for these clusters[20] suggest that all oxygen atoms are covalently bonded to metal atoms, and metal atoms and oxygen for the lowest energy structures.

### D. Hydrogen containing, oxygen rich clusters

A number of oxygen rich clusters are found to have one or two hydrogen atoms attached to them. This makes chemical sense that vanadium, niobium, and tantalum have most stable stoichiometries for $M^{+4}$ and $M^{+5}$. Thus $MO_3$, $M_2O_5$, $M_2O_6$, $M_3O_8$, etc., can readily form OH ligands to maintain these preferred valence states. This chemistry is consistent with, for example, a double oxygen bridged/three terminal oxygen atom structure for $V_2O_5$.[8,20] Added hydrogens at the terminal oxygens would maintain this chemistry as would oxobond formation (see Scheme I).




Scheme I.

Note that these hydrogen containing clusters do not occur for oxygen deficient species or for most oxygen sufficient (most stable) species, although they do appear for $M_2O_5$, $M$=V, Nb, Ta clusters.

## V. CONCLUSIONS

26.5 eV single photon ionization turns out to be an excellent diagnostic for neutral cluster distribution, in general, for all varieties of clusters from van der Waals, to hydrogen bonded, to metal, and covalent metal oxide systems. During the ionization process(es) nearly all the excess energy above the VIE of the cluster is removed by the exiting photoelectron. Where possible a comparison between 10.5 and 26.5 eV ionizations is made to show that the results of both methods of ionization are nearly identical, except that 26.5 eV ionization finds all species present in the sample. Most importantly this ionization approach has found oxygen rich clusters and oxygen rich clusters with added hydrogen

that have not previously been identified for laser ablation metal oxide clusters. Systematics for Nb and Ta systems can be established, while V containing clusters seem to have a more varied chemistry of oxygen rich and deficient clusters for all families ($M_m$) of metal containing species. Nb and Ta clusters show oxygen deficient species only for $M_m$, where m is even.

The mechanism for photoelectron removal of excess ionization energy (26.5−VIE) eV is not obvious and photoelectron spectroscopy of these processes would be very informative and useful for an understanding of the ionization mechanisms and dynamics of clusters, in general, at 26.5 eV.

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