Stoichiometric and Oxygen-Rich M_{2}O_{n−} and M_{2}O_{n} (M = Nb, Ta; n = 5–7) Clusters: Molecular Models for Oxygen Radicals, Diradicals, and Superoxides

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Supporting Information

ABSTRACT: We investigated the structures and bonding of two series of early transition-metal oxide clusters, M_{2}O_{n−} and M_{2}O_{n} (M = Nb, Ta; n = 5–7) using photoelectron spectroscopy (PES) and density-functional theory (DFT). The stoichiometric M_{2}O_{5} clusters are found to be closed shell with large HOMO–LUMO gaps, and their electron affinities (EAs) are measured to be 3.33 and 3.71 eV for M = Nb and Ta, respectively; whereas EAs for the oxygen-rich clusters are found to be much higher: 5.35, 5.25, 5.28, and 5.15 eV for Nb_{2}O_{6}, Nb_{2}O_{7}, Ta_{2}O_{6}, and Ta_{2}O_{7}, respectively. Structural searches at the B3LYP level yield triplet and doublet ground states for the oxygen-rich neutral and anionic clusters, respectively. Spin density analyses reveal oxygen radical, diradical, and superoxide characters in the oxygen-rich clusters. The M_{2}O_{5−} and M_{2}O_{6−} clusters, which can be viewed to be formed by M_{2}O_{5}^{−} + O_{2}, are utilized as molecular models to understand dioxygen activation on M_{2}O_{4−} and M_{2}O_{3} clusters. The O_{2} adsorption energies on the stoichiometric M_{2}O_{5} neutrals are shown to be surprisingly high (1.3–1.9 eV), suggesting strong capabilities to activate O_{2} by structural defects in Nb and Ta oxides. The PES data also provides valuable benchmarks for various density functionals (B3LYP, BP86, and PW91) for the Nb and Ta oxides.

1. INTRODUCTION

Structural and electronic defects are common on surfaces of transition-metal oxides, which are responsible for the interesting chemical, optical, magnetic, and catalytic properties of this class of technologically important materials.1,2 Adsorption and activation of dioxygen on metal centers are the initial steps of oxidation reactions on oxide surfaces, resulting in catalytically active oxygen radicals or superoxides.3 Among the catalytic applications of group VB oxides,4–9 the Nb oxides catalyze numerous reactions and can serve as effective catalytic supports as well.5,6 Both Nb and Ta oxides are also efficient catalytic promoters5–8 and have been considered for photocatalysts.5 Chemical processes taking place in real oxide catalysts are extremely complicated. Thus, our current understanding of the nature of active oxygen species on Nb and Ta oxides and of the interactions of oxygen with Nb and Ta centers is rather limited at the molecular level.5–9

In the past decade, increasing research efforts have been directed to gas-phase transition-metal oxide clusters,10–30 which can provide well-defined molecular models toward mechanistic insights into the complex surface processes and catalysis.31 There have been numerous gas-phase studies on Nb and Ta oxide clusters.10,15–20,27,30,32–35 Chemical reactions of charged Nb (Ta) oxide clusters with hydrocarbon molecules were reported.16,17 Single-photon VUV ionization on neutral M_{n}O_{n} (M = V, Nb, Ta) clusters showed that M_{2}O_{5}, M_{3}O_{7}, and M_{4}O_{10} clusters are most abundant.27,28,30,34 Photodissociation of cationic M_{n}O_{n}^{+} (M = V, Nb, Ta) clusters revealed enhanced stability for M_{2}O_{5}^{+}, M_{3}O_{7}^{+}, and M_{4}O_{9}^{+}.19 Infrared multiple photon dissociation (IR-MPI) spectroscopy allowed structural characterizations for a number of positively charged Nb (Ta) oxide clusters, such as Nb_{2}O_{6}^{+}, Nb_{3}O_{8}^{+}, and Ta_{2}O_{8}^{+}.10,18 We are interested in using anion photoelectron spectroscopy (PES) and computational chemistry to investigate the structures and bonding in early transition-metal oxide clusters and to discover cluster models for catalytic active centers. In a recent study, we investigated the electronic structure of the Nb_{2}O_{10}^{−} and Ta_{2}O_{10}^{−} tetrahedral cage clusters as well as polyhedral cage clusters (V_{2}O_{n})_{m}^{−} (n = 2–4).27 We also discovered δ aromacity in the Ta_{2}O_{5}^{−} cluster.28 However, the electronic structure of Nb and Ta oxide clusters remains poorly understood, and available PES studies are primarily centered on the metal-rich Nb and Ta oxide clusters.27,28,30,34

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In the current contribution, we report a combined PES and density-functional theory (DFT) study of stoichiometric and oxygen-rich M\(_2\)O\(_5\)^− and M\(_2\)O\(_n\) (M = Nb, Ta; n = 5−7) clusters in the gas phase. Well-defined PES spectra reveal large energy gaps in the Nb\(_2\)O\(_5\)^− and Ta\(_2\)O\(_5\)^− clusters and very high electron binding energies for the O-rich clusters, Nb\(_2\)O\(_n\)^− and Ta\(_2\)O\(_n\)^− (n = 6, 7). Structural searches at the B3LYP level yield open-shell ground states for all eight O-rich anionic and neutral clusters: triplets for neutrals and doublets for anions. The stoichiometric M\(_2\)O\(_n\) neutral clusters and their M\(_2\)O\(_n\)^− anions adopt singlet and doublet ground states, respectively. Electron spin density analyses show that the two M\(_2\)O\(_5\)^− anion clusters each possess a localized 4d/5d spin, giving rise to a tricoordinate M\(^{+}\) reduced center. Intriguing oxygen radical, diradical, and superoxide nature is revealed for the eight O-rich clusters, where the M\(_2\)O\(_n\) (n = 6, 7) neutral clusters appear to be as effective as their M\(_2\)O\(_n\)^− anions in the stabilization of active oxygen species, and the neutral clusters can further double the number of active oxygen species. The M\(_2\)O\(_n\)^− and M\(_2\)O\(_n\) clusters are used as molecular models to study the dioxygen activation on M\(_2\)O\(_n\)^− and M\(_2\)O\(_n\) clusters, and the O\(_2\) adsorption energies on the stoichiometric M\(_2\)O\(_n\) neutrals are found to be remarkably high (1.3−1.9 eV). These observations are in contrast to those observed in O-rich W\(_2\)O\(_8\)^−/W\(_2\)O\(_11\)^− clusters, suggesting that the Nb and Ta centers are more reactive toward O\(_2\) and can more effectively stabilize the radical, diradical, and superoxide species.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Photoelectron Spectroscopy. The experiments were carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been described previously. Briefly, the Nb (Ta) oxide clusters were produced by laser vaporization of a pure Nb (Ta) disk target in the presence of a He carrier gas seeded with 0.5% O\(_2\) and analyzed using a time-of-flight mass spectrometer. The Nb\(_2\)O\(_n\)^− and Ta\(_2\)O\(_n\)^− (n = 5−7) clusters were each mass selected and decelerated before being photodetached. The photodetachment experiments were conducted at the 193 nm (6.424 eV) photon energy from an ArF excimer laser. Effort was made to choose colder clusters (those with long resident times in the nozzle) for photodetachment, which was shown previously to be critical for obtaining high-quality PES data. Photoelectron spectra were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Au\(_3^+\), and the energy resolution of the apparatus was ΔE\(_p\)/E\(_p\) ≈ 2.5%, that is, ∼25 meV for 1 eV electrons.

2.2. Computational Methods. The DFT calculations were carried out using the hybrid B3LYP functional. The calculations are spin restricted for closed-shell molecules and spin unrestricted for open-shell species. The UB3LYP calculations turned out to have little spin contamination. The global minimum searches were performed using analytical gradients with the Stuttgart relativistic small core basis set and efficient core potential augmented with two f-type and one g-type polarization functions for Nb [ζ(f) = 0.261, 0.970; ζ(g) = 0.536] and Ta [ζ(f) = 0.210, 0.697; ζ(g) = 0.472] as recommended by Martin and Sundemann and the aug-cc-pVTZ basis set for oxygen. Scalar relativistic effects, that is, the mass velocity and Darwin effects, were taken into account via the quasi-relativistic pseudopotentials. Vibrational frequencies calculations were done to verify the nature of the stationary points. Vertical electron detachment energies (VDEs) were calculated using the generalized Koopmans’ theorem by adding a correction term to the eigenvalues of the anion. The correction term was calculated as Δ\(E = E_1 - E_2 - E_{\text{HOMO}}\) where \(E_1\) and \(E_2\) are the total energies of the anion and neutral, respectively, in their ground states at the anion equilibrium geometry and \(E_{\text{HOMO}}\) corresponds to the eigenvalue of the highest occupied molecular orbital (HOMO) of the anion. The relative energies of the low-lying structures were further evaluated using single-point calculations at the coupled cluster [CCSD(T)] level with the Nb/Ta/Stuttgart-21g/O/aug-cc-pVTZ basis sets at the B3LYP geometries. For open-shell systems, the R/UCCCSD(T) approach was used, where a restricted open-shell Hartree–Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the correlation treatment. Additional BP86 and PW91 calculations were performed on the ground-state structures for the O-rich anion clusters to test the performance of different DFT functionals. All DFT calculations were performed using the Gaussian 03 package, and the CCSD(T) calculations were done using the MOLPRO 2010.1 package.

3. EXPERIMENTAL RESULTS

The 193 nm PES data for Nb\(_2\)O\(_n\)^− and Ta\(_2\)O\(_n\)^− (n = 5−7) are shown in Figures 1 and 2, respectively. The observed spectral bands are labeled with letters (X, A, and B), and the measured adiabatic detachment energies (ADEs) and VDEs are summarized in Table 1.

3.1. Nb\(_2\)O\(_n\)^− and Ta\(_2\)O\(_n\)^−. The 193 nm PES spectrum of Nb\(_2\)O\(_5\)^− (Figure 1a) exhibits three bands (X, A, and B). The ground-state band X is weak with a relatively low binding energy (VDE = 3.58 eV; Table 1). Since no vibrational structures are resolved for band X, the ground-state ADE is evaluated by...
drawing a straight line along its leading edge and then adding the instrumental resolution to the intersection with the binding energy axis. Although this is an approximate procedure, the well-defined onset of band X allows a fairly accurate ADE value to be obtained: 3.33 ± 0.05 eV, which represents the electron affinity of the Nb$_2$O$_5$ neutral cluster. The first excited state, band A, is located at a much higher binding energy (ADE = 5.16 eV; VDE = 5.65 eV), defining a sizable energy gap of 1.83 eV as evaluated from the ADE difference between bands X and A. Band A appears broad and weak. At the highest binding energy, an intense and well-defined band B is observed (VDE = 6.32 eV).

The PES spectrum of Ta$_2$O$_5^-$ (Figure 2a) is similar to that of Nb$_2$O$_5^-$, showing two weaker bands, X (ADE = 3.71 ± 0.05 eV; VDE = 3.99 eV) and A (ADE = 5.09 eV; VDE = 5.55 eV), and an intense band B (VDE = 6.31 eV). The X–A energy gap is evaluated to be 1.38 eV for Ta$_2$O$_5^-$, which is 0.45 eV smaller than that for Nb$_2$O$_5^-$.

The PES spectra suggest that the two stoichiometric clusters, M$_2$O$_5^-$, are closed shell with sizable energy gaps (between the HOMO and the lowest unoccupied molecular orbital (LUMO). The extra electron in the M$_2$O$_5^-$ anions enters the LUMO of the neutral clusters, resulting in the relatively low electron binding energies.

3.2. Nb$_2$O$_6^-$ and Ta$_2$O$_6^-(n = 6, 7)$. Qualitatively, the PES spectra for the four O-rich species appear rather similar (Figures 1 and 2): (i) all species show extremely high electron binding energies (>5 eV); (ii) each spectrum displays two well-defined PES bands (labeled as X and A); (iii) all observed PES bands show roughly the same bandwidth (∼0.4–0.5 eV) except that the relative intensity of band A seems to increase from n = 6 to 7. The ground-state VDEs, obtained from the maximum of band X, are 5.74, 5.64, 5.57, and 5.49 eV for Nb$_2$O$_6^-$, Nb$_2$O$_7^-$, Ta$_2$O$_6^-$, and Ta$_2$O$_7^-$, respectively (Table 1). The ground-state ADEs are obtained from the well-defined onsets of band X as 5.35, 5.25, 5.28, and 5.15 eV, respectively, which also represent the electron affinities of the corresponding neutral clusters. Similarly, the VDEs for band A of the four species are obtained from the maximum of band A. All the obtained ADEs and VDEs are given in Table 1. As will be seen from the DFT calculations below, band A for all four O-rich species (and band B for the stoichiometric species) each contain contributions from multiple electronic transitions. In these cases, the experimental VDEs obtained should be viewed as average values.

4. THEORETICAL RESULTS

The optimized anion and neutral ground-state and low-lying structures (within ∼0.5 eV) at the B3LYP level are presented in Figure 3 for the M$_2$O$_n^-\text{ and } M_2O_n$ clusters and in Figures 4 and 5 for M$_2$O$_n^-\text{ and } M_2O_n$ (n = 6, 7), respectively. Alternative optimized geometries are shown in the Supporting Information (Figures S1–S12).

4.1. Nb$_2$O$_5^-\text{ and Nb}_2O_6$. Our extensive structural searches for Nb$_2$O$_5^-\text{ (Figure S1)}$ lead to the C$_2$ (1A$^0$) ground state, as shown in Figure 3a. This structure is based on a four-membered Nb$_2$O$_2$ ring motif with three additional terminal O atoms, resulting in a tetracoordinated and a tricoordinated Nb. The bridging Nb–O distances are slightly uneven (2.058 versus 1.886 Å). The terminal Nb–O distances are similar (1.74–1.75 Å). Alternative optimized Nb$_2$O$_5^-\text{ anion structures, including those with two, one, or three bridging O atoms and in different spin states (Figure S1, Supporting Information), are at least ∼1.2 eV higher in energy, suggesting the overwhelming stability of the C$_2$ (1A$^0$) structure as the global minimum of Nb$_2$O$_5^-\text{.}$

The ground state for Nb$_2$O$_6$ neutral is C$_2$ (1A$’$) (Figure 3b), differing only slightly from the global minimum of the anion. A low-lying D$_{3h}$ (A$’$) isomer is located at 0.16 eV above the ground state, which possesses three bridging O atoms (Figure 3c). Other structures are at least ∼0.9 eV higher in energy (Figure S2, Supporting Information).

4.2. Ta$_2$O$_5^-\text{ and Ta}_2O_6$. The potential energy surfaces for Ta$_2$O$_5^-\text{ and Ta}_2O_6$ are the same as those for the Nb systems. The ground state for Ta$_2$O$_5^-\text{ is C}_2 (1A’)$ (Figure 3d), which is the same as that for Nb$_2$O$_5^-\text{.}$ Similar to the Nb$_2$O$_6$ neutral, the D$_{3h}$ (A$’$) (Figure 3e) and C$_2$ (1A’)$ (Figure 3f) states for Ta$_2$O$_6$ are close in energy, except that their energy order reverses: The D$_{3h}$ (A$’$) state becomes lowest in energy for Ta$_2$O$_6$, with the C$_2$ (1A’) state being marginally higher in energy by 0.14 eV. Alternative optimized structures are at least ∼1.5 and ∼1.2 eV higher in energy for Ta$_2$O$_5^-\text{ (Figure S7, Supporting Information) and Ta}_2$O$_5$ (Figure S8, Supporting Information), respectively.

4.3. Nb$_2$O$_6^-\text{ and Nb}_2O_6$. The ground-state structure for Nb$_2$O$_6^-\text{ is } C_2 (1A’)$ (Figure 4a), which is also based on the four-membered Nb$_2$O$_2$ ring with four terminal O atoms. The bridging Nb–O distances are slightly uneven (2.054 versus 1.889 Å). Of the four terminal Nb–O distances, three are around 1.75–1.76 Å whereas the other one is quite elongated (1.936 Å)
A low-lying \( \text{Cs}(2A^0) \) state is located 0.27 eV higher in energy (Figure 4b), which is similar to the ground state in terms of atomic connectivity and characteristic bond distances. The corresponding quartet and sextet states are 3.12 and 6.78 eV above the ground state, respectively (Figure S3, Supporting Information). Other four-membered \( \text{Nb}_2\text{O}_2 \) ring-based structures, with three terminal \( \text{O} \) atoms on the same \( \text{Nb} \) center or with a terminal \( \text{O}_2 \) unit, are at least 2.4 eV higher than the ground state. Alternative optimized structures with one bridging oxygen, three bridging oxygens, or no bridging oxygen are also higher in energy (by 2.7–9.6 eV; Figure S3, Supporting Information).

A similar set of structures is optimized for the \( \text{Nb}_2\text{O}_6 \) neutral (Figure S4, Supporting Information). The \( \text{C}_2^\text{h}(3\text{Bu}) \) (Figure 4c) and \( \text{C}_2^\text{v}(3\text{B}2) \) (Figure 4d) structures are found to be virtually degenerate (within 0.02 eV), both of which are triplet states. These structures each feature two elongated \( \text{Nb}^-\text{O} \) terminal bonds (\( \sim 1.9 \) Å), differing only in their trans versus cis arrangements. The closest singlet structure, \( \text{C}_{3v}(1\text{A}_1) \), is 0.15 eV higher in energy (Figure 4e), with four bridging oxygens including a substantially elongated \( \text{O}_2 \) unit (1.457 Å). Alternative optimized neutral structures are at least 0.7 eV above the ground state (Figure S4, Supporting Information).

4.4. \( \text{Nb}_2\text{O}_7^- \) and \( \text{Nb}_2\text{O}_7^+ \). The ground state of \( \text{Nb}_2\text{O}_7^- \) is \( \text{Cs}(2A^0) \) (Figure 4f), which can be viewed as built from the \( \text{Cs}(2A^0) \) ground-state structure of \( \text{Nb}_2\text{O}_6^- \) by replacing the elongated terminal oxygen with an \( \text{O}_2 \) unit. Alternative optimized anion structures are at least 1 eV higher in energy (Figure S5, Supporting Information). The neutral ground state, \( \text{Cs}(3A^0) \) (Figure 4g), shows similar structural characteristics relative to its anion, except that one terminal \( \text{Nb}^-\text{O} \) distance is elongated (1.907 Å). A similar \( \text{Cs}(3A^0) \) state is located 0.35 eV above the neutral ground state (Figure 4h), whereas alternative neutral structures are much higher in energy (>0.8 eV; Figure S6, Supporting Information).

4.5. \( \text{Ta}_2\text{O}_n^- \) and \( \text{Ta}_2\text{O}_n^+ (n = 6, 7) \). The potential energy surfaces of \( \text{Ta}_2\text{O}_6^- \) and \( \text{Ta}_2\text{O}_n^- (n = 6, 7) \) (Figures S9–S12, Supporting Information) are similar to those of the \( \text{Nb}_2\text{O}_6^- \) and \( \text{Nb}_2\text{O}_7^+ \) counterparts. The calculated ground-state and low-lying...
structures for Ta$_2$O$_n^-$ and Ta$_2$O$_n$ (n = 6, 7) are summarized in Figure 5, which show one-to-one correspondence to those of Nb$_2$O$_n^-$ and Nb$_2$O$_n$ (Figure 4), except for very minor changes in bond angles and bond distances. It is noted that while the majority of terminal and bridging M–O bonds in the ground-state structures show slight expansions from Nb to Ta, the elongated M–O bonds undergo slight contractions and the O–O distances in the O$_2$ units show slight expansions, hinting that the Ta centers can probably stabilize the unusual oxygen species and activate O$_2$ better.
5. COMPARISON BETWEEN EXPERIMENT AND THEORY

5.1. Nb₂O₅⁻ and Ta₂O₅⁻. The C₁ (A') structures (Figure 3a and 3d) are clearly the ground states for Nb₂O₅⁻ and Ta₂O₅⁻, with alternative structures (Figures S1 and S7, Supporting Information) being at least ~1.2 and ~1.5 eV higher in energy, respectively. The calculated ground-state VDEs at the B3LYP level are 3.79 eV for Nb₂O₅⁻ and 4.05 eV for Ta₂O₅⁻ (Table 1), which are compared to the experimental values of 3.58 and 3.99 eV, respectively. The B3LYP method appears to slightly overestimate the binding energies with an error of 0.21 and 0.06 eV, respectively. The simulated PES spectra for Nb₂O₅⁻ (Figure 6a) and Ta₂O₅⁻ (Figure 6d) agree well with the experimental data, reproducing the characteristic X—A energy gaps and the overall patterns.

5.2. Nb₂O₆⁻ and Ta₂O₆⁻ (n = 6, 7). All M₂O₆⁻ (M = Nb, Ta; n = 6, 7) clusters are O-rich species, consistent with the observed high electron affinities for the neutrals: 5.35, 5.25, and 5.15 eV for Nb₂O₆, Nb₂O₇, and Ta₂O₆, respectively (Table 1), which are among the highest in gas-phase molecules,⁵ insurering that these neutral clusters are extremely

![Figure 6. Simulated photoelectron spectra (red curves) for Nb₂O₅⁻ and Ta₂O₅⁻ (n = 5–7) based on their ground-state structures, compared to experimental spectra (black curves). The simulations are done by fitting the distribution of calculated vertical detachment energies with unit-area Gaussian functions of 0.1 eV width.](image-url)

### Table 2. Relative Energies of the Low-Lying States of the M₂O₆⁻ (M = Nb, Ta; n = 5–7) Clusters at the B3LYP Level (within ~0.5 eV), and Comparisons with Those from the CCSD(T) Single-Point Calculations at the B3LYP Geometries

<table>
<thead>
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<th>electronic state</th>
<th>B3LYP a,b</th>
<th>CCSD(T) c,d</th>
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<tr>
<td>Nb₂O₅⁻</td>
<td>C₁ (A')</td>
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<tr>
<td>Ta₂O₅⁻</td>
<td>D₃h (A₁g)</td>
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<tr>
<td>Nb₂O₆⁻</td>
<td>C₁ (A')</td>
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</tr>
<tr>
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<td>0.00</td>
</tr>
<tr>
<td>Nb₂O₇⁻</td>
<td>C₁ (A')</td>
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</tr>
<tr>
<td>Ta₂O₇⁻</td>
<td>C₁ (A')</td>
<td>0.33</td>
</tr>
</tbody>
</table>

a All energies are in eV. b Optimized at the B3LYP/Nb,Ta/Stuttgart+2f1g/O/aug-cc-pVTZ level. c Single-point energy at the CCSD(T)/Nb, Ta/Stuttgart+2f1g/O/aug-cc-pVTZ//B3LYP/Nb,Ta/Stuttgart+2f1g/O/aug-cc-pVTZ level.

4.6. CCSD(T) Single-Point Calculations for Low-Lying Cluster Structures. The relative energies for the low-lying M₂O₆⁻ and M₂O₇⁻ (M = Nb, Ta; n = 5–7) cluster structures (within ~0.5 eV at B3LYP level; Figures 3–5) were further calculated using single-point CCSD(T) calculations at the B3LYP geometries. The results are summarized in Table 2. It can be seen that the energetics from the CCSD(T) calculations are in line with the B3LYP results except for the ground state of Nb₂O₆⁻. Further theoretical calculations with more sophisticated methods, such as full CCSD(T) structural optimization, may be necessary to resolve the true ground state of Nb₂O₆⁻ but these are computationally not feasible for us currently. It should be stressed that the current experiment starts with the Nb₂O₆⁻ cluster anion and, upon photodetachment, only probes the C₃₃ (B₁u) and C₂₄ (B₂u) final states of the Nb₂O₆⁻ neutral cluster. We will not be able to access the Nb₂O₆⁻ C₂₄ (A₁g) state even if it is indeed slightly lower in energy. Thus, we believe the B3LYP results are generally solid for our discussion below.
strong oxidizers. The ground-state VDEs for Nb2O6−, Ta2O6−, Ta2O7−, and Ta3O7− are measured to be 5.74, 5.64, 5.57, and 5.49 eV, respectively. For comparison, the calculated VDEs at the B3LYP level for the anion ground-state structures are 5.61, 5.51, 5.49, and 5.43 eV along the same series, which nicely correlate with the experimental trend. The computational data consistently underestimates the experimental values by marginal errors (0.13 – 0.17 eV). The simulated PES spectra for the four clusters agree well with the experimental data (Figure 6). We found that band A involves multiple electronic transitions with close binding energies (see Table S1 in the Supporting Information), and the average of the calculated VDEs agrees perfectly with the experimental measurements (errors = 0.01 – 0.09 eV). The frontier MOs for all four anions consist primarily of O 2p atomic orbitals from the terminal O atoms (M=O), consistent with their similar experimental PES patterns. Overall, the agreement between experimental and theory is excellent, lending considerable credence to the identified anion ground-state structures and the suitability of the B3LYP method.

6. DISCUSSION

6.1. Radicals, Diradicals, and Superoxides in M2O2− and M2O− (M = Nb, Ta; n = 6, 7). The ground-state structures for the O-rich M2O2− and M2O− (M = Nb, Ta; n = 6, 7) clusters are similar in terms of atomic connectivity, symmetry and electronic state, and bond distances (Figures 4 and 5), consistent with their similar PES patterns (Figures 1 and 2). An examination of the bond distances between Nb (Ta) and O shows the following. (i) The bridging bond distances average at ~1.96 Å for both Nb and Ta, and typical terminal M–O bonds average at ~1.74 Å for Nb and ~1.76 Å for Ta, which can be roughly attributed to M–O single bonds and M=O double bonds, respectively. (ii) The elongated M–O terminal bonds average at ~1.92 Å for Nb and ~1.90 Å for Ta, which are substantially longer than the M=O double bonds and may be assigned as M=O single bonds, that is, single bonds between Nb (Ta) centers and oxygen radicals (O•). (iii) The distances between Nb (Ta) centers and the terminal O2 units average at ~2.14 Å for both Nb and Ta. These are assigned as the M=O• bonds involving a superoxide (O2•−) unit, in which the bond order between the Nb (Ta) center and the O atom may be formally considered as 0.5. (iv) The O=O bond order in the superoxide units is 1.5, whose calculated distances average at ~1.33 Å for Nb and ~1.34 Å for Ta, in line with the gas-phase value for superoxide (1.341 Å).3 Following these bond order assignments, the chemical bonding in the clusters can be understood on the basis of Lewis structures.

The structures of all eight O-rich anion and neutral clusters are based on the M2O2 four-membered ring motif, in which each Nb (Ta) center is tetracoordinated with two bridging O units and two terminal O or O2 units (Figures 4 and 5). In their favorite (Ta) center is tetracoordinated with two bridging O units and may be assigned as M=O• bonds involving a superoxide (O2•−) unit, in which the bond order between the Nb (Ta) center and the O atom may be formally considered as 0.5. (iv) The O=O bond order in the superoxide units is 1.5, whose calculated distances average at ~1.33 Å for Nb and ~1.34 Å for Ta, in line with the gas-phase value for superoxide (1.341 Å).3 Following these bond order assignments, the chemical bonding in the clusters can be understood on the basis of Lewis structures.

The four oxygen-rich neutral clusters (Figure 7, right column) each possess two unpaired spins, which form diradical species (O•− + O•−) in Nb2O6 and Ta2O6 and (O• + O2•−) in Nb2O7 and Ta2O7. Note that due to relativistic effects in the 5d element,51 there is a slight increase of d electron in the spin density from Nb to Ta. Oxygen radicals and superoxides have been widely discussed in the oxide surface chemistry5 and in transition-metal oxide clusters.10–13,25,26 Such species are expected to be highly reactive toward H abstraction or other oxidation reactions and may play significant roles in the surface chemistry of Nb and Ta oxides. However, report of these transient species on Nb and Ta oxide surfaces has been elusive. In gas-phase clusters, an IR-MPI study assigned a superoxide (O2•−) unit in the cationic Nb2O6+ cluster,10 whereas a combined IR-MPI and DFT study by Sauer and co-workers14 with the aid of experimental PES data,32 revealed superoxides in valent isoelectronic V2O7− and V2O7− clusters.

Other types of active oxygen species can also be found in the Nb (Ta) oxide clusters. For example, the low-lying isomeric C2v (1A1) states of Nb2O6 and Ta2O6 (Figures 4e and 5e) possess a...
highly activated O₂ unit (O—O bond distances = 1.457–1.474 Å) in a bridging fashion, which is peroxide in nature (O₂⁻ = 1.49 Å)³ and may be viewed as the fusion of two O* radicals. These structures can be constructed from the C₂₅ (¹B₂) structures (Figures 4d and 5d) by bending two terminal O* radicals toward each other and pairing up the two unpaired spins, at the expense of a small overall energy penalty (0.1–0.4 eV). In fact, the C₂₅ (¹A₁) structures can be described as classical Lewis structures, in which each Nb (Ta) center forms three M—O single bonds and one M=O double bond and the peroxide unit possesses an O—O single bond. These classical M₂O₆ C₃₅ (¹A₁) structures, along with the classical M₂O₆D₅₆ (¹A₁') structures (Figure 3c and 3e), help define the “ideal” bridging M—O and terminal M=O bond distances in the gas phase, which average at 1.97, 1.98, 1.72, and 1.74 Å for Nb—O, Ta—O, Nb=O, and Ta=O bonds, respectively. A direct implication from these values is that those bridging M—O and terminal M=O bonds in the ground-state structures of M₂O₅— and M₂O₆ (M = Nb, Ta, n = 5–7; Figures 3–5) deviate somewhat from the ideal single and double bonds, as anticipated.

6.2. M₂O₇ and M₂O₆ as Molecular Models for Dioxygen Activation by M₂O₅⁻/⁰: M₂O₅⁻/⁰ + O₂ → M₂O₇⁻/⁰. The observations of superoxide species in M₂O₆⁻ and M₂O₆ provide us with an excellent opportunity to study the activation of O₂ by the M₂O₅— and M₂O₆ clusters, which is of fundamental interest in the surface chemistry of Nb and Ta oxides.⁵—⁹ The M₂O₇⁻/⁰ clusters may be formed by M₂O₅—/⁰ + O₂ as schematically illustrated in Figure 8. The energetics of the O₂ addition reactions are evaluated at the B3LYP level:

\[
\begin{align*}
\text{Nb}_2\text{O}_5^{-} (C_{\text{O}_2}^{\text{2A}^\prime}) + & \text{O}_2 \rightarrow \text{Nb}_2\text{O}_7^{-} (C_{\text{O}_2}^{\text{2A}''}) - 3.00 \text{ eV} \quad (1) \\
\text{Nb}_2\text{O}_5^{-} (C_{\text{O}_2}^{\text{A}^\prime}) + & \text{O}_2 \rightarrow \text{Nb}_2\text{O}_7^{-} (C_{\text{O}_2}^{\text{3A}''}) - 1.34 \text{ eV} \quad (2) \\
\text{Ta}_2\text{O}_5^{-} (C_{\text{O}_2}^{\text{2A}^\prime}) + & \text{O}_2 \rightarrow \text{Ta}_2\text{O}_7^{-} (C_{\text{O}_2}^{\text{2A}''}) - 3.14 \text{ eV} \quad (3) \\
\text{Ta}_2\text{O}_5^{-} (C_{\text{O}_2}^{\text{A}^\prime}) + & \text{O}_2 \rightarrow \text{Ta}_2\text{O}_7^{-} (C_{\text{O}_2}^{\text{3A}''}) - 1.90 \text{ eV} \quad (4)
\end{align*}
\]

The M₂O₇⁻ anions are shown to have a localized spin on the tricoordinate metal site, which is effectively a reduced M⁺⁺ defect site (Figure 7a and 7b). An O₂ molecule readily chemisorbs at the M⁺⁺ site via charge transfer (Figure 8a), giving rise to a superoxide (O₂⁻) species with a substantial chemisorption energy (3.00 eV for M = Nb; 3.14 eV for M = Ta). Consequently, the dioxygen is activated as shown from the elongated O—O distances: 1.332–1.337 Å in O₂⁻ (Figures 4f and 5f) versus 1.21 Å in free O₂.³

The O₂ adsorption energies on neutral M₂O₆ clusters are calculated to be 1.34 eV for M = Nb and 1.90 eV for M = Ta. These large adsorption energies are surprising, considering the fact that M₂O₆ are closed-shell stoichiometric clusters and are expected to be relatively inert. The large adsorption energies are due to the formation of triplet M₂O₇ products, which are essentially diradicals. Thus, the M₂O₆ reactions with O₂ to form M₂O₇ can be viewed to involve promotion of an electron from O 2p to the metal d orbitals, as schematically shown in Figure 8b. This promotion would induce a large energy barrier for the O₂ adsorption process. This energy barrier is the HOMO—LUMO gap, as measured from the PES spectra (Figures 1a and 2a), ~1.8 and ~1.4 eV for NbO₂ and Ta₂O₅, respectively. Even though this is a substantial barrier, it is much lower compared to those in the bulk oxides (3.4 eV for Nb₂O₅; 3.5–4.5 eV for Ta₂O₅)³³,³⁴ or the corresponding tetrahedral cage M₂O₁₀ clusters (3.88 eV for Nb₂O₁₀; 3.87 eV for Ta₂O₁₀).²⁷ In photocatalysis, for example, such barriers for the neutral M₂O₅ clusters are relatively small and can be easily overcome by visible or near-infrared photons.

Thus, the M₂O₅ (M = Nb, Ta) clusters are very different from the stoichiometric W₂O₆ cluster, which only forms a van der Waals complex with O₂ in W₂O₈ via physisorption (<0.1 eV),²⁶ even though W₂O₈ contains a superoxide analogous to that in M₂O₇— (M = Nb, Ta). Note that, however, the strengths for typical M=O double bonds are comparable for the three elements: 7.53, 8.70, and 7.46 eV for Nb=O, Ta=O, and W=O, respectively.⁵⁵ The O₂ chemisorption energies on the 3d counterparts, V₂O₅ and Zr₂O₂, are calculated (at the same level) to be 1.89 and 0.92 eV, respectively, which are markedly lower than those for Nb (Ta) oxides but differ qualitatively from those for W oxides.⁵⁶ Therefore, the Nb and Ta oxide clusters appear to possess superior abilities to activate O₂ due in part to the existence of tricoordinate Nb (Ta) sites, which facilitate stronger interactions with O₂. The current results may shed light on the surface chemistry of Nb (Ta) oxides, such as their remarkable properties as catalytic promoters, which are poorly understood at the molecular level.⁵—⁹

6.3. Benchmarks of DFT Methods. One of the values of cluster studies is to provide quantitative data to verify theoretical methods.⁵⁷,⁵⁸ The current PES data yield relatively accurate electron binding energies for the Nb and Ta oxide clusters (Table 1), which can be utilized to benchmark the performance of various density functionals. The experimental ground-state VDEs for the four oxygen-rich M₂O₅⁻⁻ (M = Nb, Ta; n = 6, 7) clusters are compared with the DFT results at the B3LYP, BP86, and PW91 levels (Figure 9). The BP86 and PW91 functionals are shown to severely underestimate the binding energies and fail to reproduce the trend of the binding energies. In particular, the BP86 functional fails severely in the case of Ta₂O₇⁻⁻ (by 0.40 eV), whereas PW91 fails for both Nb₂O₇⁻⁻ and Ta₂O₇⁻⁻ (by 0.49 and 0.46 eV, respectively). It seems that the superoxide species in Nb₂O₇⁻⁻ and Ta₂O₇⁻⁻ pose greater challenges for pure DFT methods such as BP86 and PW91, likely associated with their deficiency in describing the O—O bonding. On the other hand, the hybrid B3LYP functional works well for all species, faithfully reproducing the experimental binding energy trend along the series with a consistent, small error (0.13–0.17 eV). Thus, the B3LYP method performs better for Nb and Ta oxide clusters,
both qualitatively and quantitatively. This information should be valuable for computational modeling of the bulk and surface properties of Nb/Ta oxides.

7. CONCLUSIONS

We studied the electronic structure of stoichiometric and O-rich Nb and Ta oxide clusters, $M_2O_n^-$ and $M_2O_n$, ($M = Nb$, Ta; $n = 5–7$), via anion photoelectron spectroscopy and density-functional calculations. Large HOMO–LUMO gaps are observed for the stoichiometric clusters, whereas very high electron binding energies are measured for the O-rich clusters (>5.1 eV). Structural searches at the B3LYP level show that all the O-rich clusters are open-shell: doublets for the anions and triplets for the neutrals. Spin density analyses reveal oxygen radical, diradical, and superoxide characters for the O-rich anion and neutral species. The $M_2O_7^-$ and $M_2O_5^-$ clusters both contain an activated $O_2$ unit and can be viewed as formed by $O_2$ chemisorption to the stoichiometric clusters, $M_2O_4$ and $M_2O_3$, respectively. The $O_2$ adsorption on $M_2O_5^-$ yields $M_2O_7^-$ with a superoxide unit (via charge transfer). The adsorption energies on the stoichiometric $M_2O_5$ neutrals are surprisingly high (1.3–1.9 eV), yielding the $M_2O_5$ diradicals, which also contain an activated $O_2$. The current results suggest that structural defects in Nb and Ta oxides should possess superior properties for $O_2$ activation. The experimental data have also been used to benchmark the performance of B3LYP, BP86, and PW91 functionals, and B3LYP is found to perform much better for Nb and Ta oxide systems.

ASSOCIATED CONTENT

Supporting Information. Observed vertical detachment energies for $Nb_2O_6^-$ and $Ta_2O_6^-$ ($n = 5–7$) clusters and their comparison with those calculated at the B3LYP level (Table S1), alternative optimized anion and neutral cluster structures at the B3LYP level (Figures S1–S12) and their Cartesian coordinates (Tables S2 and S3), and complete ref 48. This material is available free of charge via the Internet at http://pubs.acs.org.

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