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# FRONTIERS ARTICLE

# Probing the electronic structure of early transition metal oxide clusters: Molecular models towards mechanistic insights into oxide surfaces and catalysis

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#### ABSTRACT

Selected recent works from the authors' laboratory on the intrinsic electronic and structural properties of early transition metal oxide clusters are reviewed. These clusters provide well-defined molecular models pertinent to mechanistic understandings of complex oxide surface chemistry and catalysis. The energy gap evolution with cluster size was probed for the stoichiometric  $(TiO_2)_n^-$ ,  $(V_2O_5)_n^-$ , and  $(CrO_3)_n^-$  clusters, and each system was shown to approach the band gap of bulk oxides in a unique way. A variety of other model clusters have been characterized, such as the oxygen radical or diradical on a single  $W^{6+}$  site in  $WO_4^-/WO_4$ , the superoxide  $(WO_3)_n(O_2^-)$  complexes for dioxygen activation, and terminal versus bridging oxygen in  $M_3O_2^-$  (M = Nb, Ta) clusters. Novel chemical bonding has been observed in a number of oxide clusters. The  $W_3O_9^-$  and  $W_3O_9^{-2-}$  clusters were found to possess d-orbital aromaticity, whereas  $\delta$ -aromaticity was discovered in the Ta<sub>3</sub>O<sub>3</sub><sup>--</sup> cluster.

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### 1. Introduction

There have been increasing interests in the past decade towards a molecular-level understanding of early transition metal oxide surface chemistry and catalysis, using advanced experimental and computational tools and model systems [1]. These interests are motivated by the importance and challenge to elucidate the catalytic mechanisms and tailor-design new oxide catalysts. Gasphase cluster model studies have emerged as a valuable approach towards mechanistic insights into the complex surface chemistry and catalytic processes of early transition metal oxides and have been actively pursued [2-25]. The cluster model studies have several advantages. First, clusters are finite in size, allowing their detailed structures and atomic connectivity to be obtained. These well-defined systems are ideal models for the investigation of catalytic elementary steps and reactive intermediates. Second, the compositions of oxide clusters can be controlled and tuned, making it possible for systematic studies. In particular, non-stoichiometric clusters can be readily prepared, which may mimic electronic or structural defect sites and catalytic active centers. Third, sizedependent studies help bridge the gap between isolated systems and extended oxide surfaces and bulk materials, for which spectroscopic information is difficult to obtain due to sample inhomogenity. Most importantly, clusters can provide quantitative data to verify and benchmark theoretical methods.

In this Letter, we briefly summarize our recent anion photoelectron spectroscopy (PES) studies of early transition metal oxide

\* Corresponding author. E-mail address: Lai-Sheng\_Wang@brown.edu (L.-S. Wang). clusters [26-45]. We will primarily focus on the oxides of groups IVB (Ti), VB (V, Nb, and Ta), and VIB (Cr and W) elements. Among the broad technological applications, V, Cr, and W oxides are responsible for numerous industrial catalytic processes [46-48], while Nb and Ta oxides show remarkable properties as catalytic promoters [49-51]. W oxides are also utilized as electrochromic smart windows [52] and as gas sensors [53], and Ti, Nb, Ta, and W oxides are exploited as photocatalysts [54-56]. The long-term goal of cluster model studies is to provide a molecular-level understanding of all these processes. Our approach is to combine PES with density-functional theory (DFT) calculations, which has been proved to be powerful in investigating the electronic structure and chemical bonding in a variety of clusters and molecules [57–70]. We have shown that transition metal oxide clusters are versatile molecular models, whose intrinsic electronic and structural properties can offer mechanistic insights relevant to oxide surface processes and catalysis. We will focus on three specific topics: (i) stoichiometric oxide clusters and the evolution of their energy gap with cluster size; (ii) oxide clusters as possible molecular models for surface defect sites and catalysts; (iii) novel chemical bonding in O-deficient clusters: d-orbital aromaticity and  $\delta$ aromaticity.

#### 2. Experimental method

All our experimental studies involve a magnetic-bottle time-offlight PES apparatus equipped with a laser vaporization cluster source, details of which were described previously [71,72]. Oxide clusters are usually produced using a helium carrier gas seeded with  $O_2$ . Negatively charged clusters are extracted from the cluster





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beam perpendicularly and are analyzed by time-of-flight mass spectrometry. Clusters of interest are selected and decelerated before being photodetached by a laser beam. A variety of laser photon energies are available for photodetachment: 532 nm (2.331 eV), 355 nm (3.496 eV), and 266 nm (4.661 eV) from a Nd:YAG laser, 193 nm (6.424 eV) from an ArF excimer laser, and 157 nm (7.866 eV) from an F2 excimer laser. Effort was made to choose colder clusters for photodetachment, which has been shown to be important for obtaining high quality PES data [73–76]. Photoemitted electrons are collected by the magnetic-bottle at nearly 100% efficiency and analyzed in a 3.5 m long electron time-of-flight tube. The photoelectron spectra are calibrated using the known spectra of Rh<sup>-</sup> and Au<sup>-</sup>, and the energy resolution of the apparatus is  $\Delta$ KE/KE ~ 2.5%, that is, ~25 meV for 1 eV electrons.

#### 3. Stoichiometric oxide clusters

Stoichiometric metal oxides are either insulators or semiconductors with intrinsic band gaps. However, relatively little is known about how the energy gaps evolve as a function of size in metal oxide clusters. We have obtained PES data for several cluster systems,  $(TiO_2)_n^-$ ,  $(V_2O_5)_n^-$ , and  $(CrO_3)_n^-$  (Figures 1–3), yielding direct energy gap information in the small size regime [37,39,41].

3.1.  $(TiO_2)_n^-$  (n = 1-10)

The  $(\text{TiO}_2)_n^-$  (n = 1-10) clusters represents the first stoichiometric oxide cluster system, whose electronic structure has been systematically probed [37,77]. Figure 1 shows their PES spectra taken at 193 and 157 nm photon energies, where the 193 nm spectra are shown as insets for the lowest binding energy feature only. Each  $(\text{TiO}_2)_n^-$  cluster exhibits a weak low binding energy band (X), followed by an energy gap and more intense and congested PES features at higher binding energies. A second band (A) is clearly resolved for n = 1 and 2, but it appears to broaden and becomes a shoulder for n > 2. The adiabatic detachment energy (ADE) of band X, which also represents the electron affinity of the neutral cluster, increases rapidly with size only for n = 1-3 (by 0.5–0.7 eV per TiO<sub>2</sub> unit) and levels off for n = 3-10 (by 0.1–0.2 eV per TiO<sub>2</sub> unit).

In the stoichiometric  $(TiO_2)_n$  clusters, all the Ti 3d/4s valence electrons can be considered to be transferred to the O 2p orbitals, giving rise to the formal Ti<sup>4+</sup> and O<sup>2-</sup> oxidation states. All occupied frontier molecular orbitals (MOs) in the  $(TiO_2)_n$  neutrals are primarily O 2p in nature, whereas in the  $(TiO_2)_n^{-1}$  anion the extra electron occupies a Ti 3d based MO. Thus, in the PES spectra of  $(TiO_2)_n^{-1}$ , bands X and A correspond to Ti 3d and O 2p based electronic transitions, respectively, which are related to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the  $(TiO_2)_n$  neutral, analogous to the empty Ti 3d conduction band and O 2p valence band in bulk  $TiO_2$  oxides (band gap: 3.0 eV for rutile and 3.2 eV for anatase [54]). The ADE difference between bands X and A represents strictly the excitation energy of the lowest triplet state in the  $(TiO_2)_n$  cluster, which is also an experimental measure of its HOMO-LUMO energy gap. As shown in Figure 4a, the X-A energy gap displays an even-odd alternation from n = 1-4, increases rapidly from n = 3 to 6, and reaches the bulk limit at n = 6 and stays nearly constant up to n = 10 within our experimental uncertainties.

The rapid approach to the bulk band gap in the  $(TiO_2)_n$  clusters in surprising. This observation is consistent with previous optical experiments on TiO<sub>2</sub> nanoparticles [78], which showed that no quantum confinement down to 1 nm particles. These results suggest a small exciton radius for TiO<sub>2</sub>, in agreement with the observation that the extra electron in the  $(TiO_2)_n^-$  clusters is localized [37].



**Figure 1.** Photoelectron spectra of  $(TiO_2)_n^-$  (n = 1-10) at 193 nm (6.424 eV) and 157 nm (7.866 eV) [37]. The 193 nm spectra are shown as insets.

3.2.  $(V_2O_5)_n^-$  (*n* = 2–4)

Figure 2 (left column) shows the PES spectra of  $(V_2O_5)_n^-$  (n = 2-4) at 193 and 157 nm, where the 193 nm spectra are shown as insets [39]. The PES spectra of  $Nb_4O_{10}^-$  and  $Ta_4O_{10}^-$  are presented in Figure 2 (right column), along with those of  $V_4O_{10}^-$  for comparison. The 157 nm spectra show the ground-state transition as a relatively weak feature, followed by a large energy gap and more intense features at very high binding energies (>6.7 eV). The ground-state ADEs for all three  $(V_2O_5)_n^-$  clusters are quite high,



**Figure 2.** Photoelectron spectra of  $V_4O_{10}^-$ ,  $V_6O_{15}^-$ , and  $V_8O_{20}^-$  at 193 and 157 nm (left column) and comparison of the photoelectron spectra of  $V_4O_{10}^-$ ,  $Nb_4O_{10}^-$ , and  $Ta_4O_{10}^-$  at 193 and 157 nm (right column) [39]. The 193 nm spectra are shown as insets.

with a relatively small size-dependent increase of only 0.06 and 0.13 eV per V<sub>2</sub>O<sub>5</sub> unit. The ADE of band *A* is more sensitive to cluster size and increases by ~0.25 eV per V<sub>2</sub>O<sub>5</sub> unit. The *X*-*A* energy gap thus shows a moderate size-dependence from 2.58  $\rightarrow$  2.78  $\rightarrow$  2.90 eV along the (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> (n = 2-4) series (Figure 4b). Interestingly, all these energy gaps exceed that of bulk V<sub>2</sub>O<sub>5</sub> oxide (~2.3 eV [79]).

For the  $M_4O_{10}^-$  (M = V, Nb, Ta) series (Figure 2, right column), Nb<sub>4</sub>O<sub>10</sub><sup>-</sup> and Ta<sub>4</sub>O<sub>10</sub><sup>-</sup> show nearly identical PES spectra with much lower ground-state ADEs (Nb<sub>4</sub>O<sub>10</sub><sup>-</sup>: 2.87 eV; Ta<sub>4</sub>O<sub>10</sub><sup>-</sup>: 2.98 eV) relative to V<sub>4</sub>O<sub>10</sub><sup>-</sup> (4.26 eV). The ADEs of band *A* are similar for all three M<sub>4</sub>O<sub>10</sub><sup>-</sup> clusters. Consequently, the 4d and 5d species possess nearly identical energy gaps (Nb<sub>4</sub>O<sub>10</sub><sup>-</sup>: 3.88 eV; Ta<sub>4</sub>O<sub>10</sub><sup>-</sup>: 3.87 eV), which are much larger than that for V<sub>4</sub>O<sub>10</sub><sup>-</sup> (2.58 eV). The main reason for this trend is because the 3d orbitals are in general more contracted than the 4d/5d orbitals, resulting in the higher ground-state ADE in V<sub>4</sub>O<sub>10</sub><sup>-</sup> relative to those in Nb<sub>4</sub>O<sub>10</sub><sup>-</sup> and Ta<sub>4</sub>O<sub>10</sub><sup>-</sup>. Note that the observed energy gap for Nb<sub>4</sub>O<sub>10</sub><sup>-</sup>, and to some extent for Ta<sub>4</sub>O<sub>10</sub><sup>-</sup> as well, is also greater than the band gap of the bulk oxide (Nb<sub>2</sub>O<sub>5</sub>: 3.4 eV [80,81]; Ta<sub>2</sub>O<sub>5</sub>: 3.5–4.5 eV [82–86]).

3.3.  $(CrO_3)_n^-$  (n = 1-5)

The 193 and 157 nm PES spectra of  $(\text{CrO}_3)_n^-$  (n = 1-5) are presented in Figure 3 [41]. The ground-state ADE (band X) increases sharply (by 0.59 eV) only from n = 1-2, beyond which it increases almost linearly with a much smaller slope of 0.17–0.19 eV per CrO<sub>3</sub> unit for n = 2-5. The ADE of band A also shows a large increase (by 1.23 eV) from n = 1-2 and the increase becomes smaller for n = 2-5 (0.20–0.53 eV per CrO<sub>3</sub> unit), thus opening up the energy gap with increasing cluster size (Figure 4c). Interestingly, the en-

ergy gap seems to level off at n = 4 and reaches an asymptotic value of ~2.2 eV. Although bulk CrO<sub>3</sub> is structurally well-characterized, its optical properties remain elusive. Three widely different band gap values of 2.25, 3.14, and 4.32 eV were reported [87,88]. The main experimental difficulty with the bulk band gap measurements is the existence of various stable and intermediate Cr oxide phases [89]. These include the three principal oxides (CrO<sub>3</sub>, CrO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub>), which possess distinct crystal structures and different electronic and optical properties, but are readily interchangeable (e.g., via changes in temperature). The gas-phase cluster data (Figure 4c) suggests that the smaller value reported for the bulk may be closer to the true band gap for bulk CrO<sub>3</sub>.

The rapid convergence to the bulk band gap in the  $(CrO_3)_n^{-1}$ clusters may be associated with the cyclic ring structures of  $(CrO_3)_n^-$  and  $(CrO_3)_n$ , as shown in Figure 5. These clusters can be viewed as tetrahedral CrO<sub>4</sub> units fused together by sharing corners, each Cr center being tetracoordinated by two terminal O atoms (Cr=O) and two bridging O atoms (Cr-O). In a similar fashion, the bulk CrO<sub>3</sub> crystal is composed of infinite chains of corner-sharing CrO<sub>4</sub> tetrahedra, in which adjacent chains are held together by van der Waals forces [90]. Upon increasing cluster size, the structural parameters of  $(CrO_3)_n$  clusters quickly converge to those of bulk CrO<sub>3</sub>. For example, the Cr=O bond distance is close to that of the bulk (1.599 Å) even for the dimer (1.576 Å) and it remains virtually constant for n = 2-5. The Cr–O bond distance shrinks slightly from n = 2 to n = 4 (1.782, 1.773, 1.765 Å) and becomes constant for  $n \ge 4$ , as compared to the bulk value of 1.748 Å. The tetrahedral bond angles ( $\angle O=Cr=O$  and  $\angle O-Cr-O$ ) in the clusters follow a similar trend and rapidly converge to the ideal tetrahedral bond angle of 109.5°. The bridging bond angle ( $\angle$ Cr–O–Cr) in



**Figure 3.** Photoelectron spectra of  $(CrO_3)_n^-$  (n = 1-5) at (a) 193 nm and (b) 157 nm [41].



**Figure 5.** Optimized ground-state structures of  $(CrO_3)_n$  at the PW91 level. The Cr–O bond distances (in Å) and the  $\angle O$ –Cr–O bond angles (°) are shown [41].

 $(CrO_3)_n$  varies from  $120^\circ \rightarrow 135^\circ \rightarrow 142^\circ$  (*n* = 3–5). It reaches an asymptotic value of ~145° (instead of 180°), similar to the

 $\angle$ Cr–O–Cr bridging bond angle of 143° in the bulk [90]. The extra electron in (CrO<sub>3</sub>)<sub>n</sub><sup>-</sup> (*n* = 2–5) is shown to be primarily delocalized over the Cr centers, subject to minor Jahn–Teller distortions in the Cr<sub>3</sub>O<sub>9</sub><sup>-</sup> and Cr<sub>5</sub>O<sub>15</sub><sup>-</sup> cases. Indeed, as mentioned above, the



**Figure 4.** Observed energy gaps of oxide clusters as a function of size (solid dots) from anion photoelectron spectra of (a)  $(TiO_2)_n^-$ , (b)  $(V_2O_5)_n^-$ , and (c)  $(CrO_3)_n^-$ . The band gaps of their bulk oxides (horizontal dashed lines) are shown for comparison.

ground-state ADEs exhibits a sharp increase only from  $CrO_3^-$  to  $Cr_2O_6^-$ , hinting that electron delocalization over multiple Cr centers is the prime reason for the additional stabilization of the extra electron in the cluster anions.

#### 4. Cluster models for oxide surfaces and catalysts

# 4.1. The $(TiO_2)_n^-$ clusters: molecular models for $Ti^{3+}$ sites

The PES spectra for  $(TiO_2)_n^-$  are rather broad beyond n = 3 (Figure 1). The width of the ground-state transition (X) defines a substantial reorganization energy of ~0.4-1.2 eV, as evaluated from the difference between the ADE and vertical detachment energy (VDE). Our PES studies of Ti, V, Cr, Al, and Si oxide clusters [37,39,41,91,92] have established a correlation between the cluster reorganization energy and the degree of electron localization. The broad PES features for  $(TiO_2)_n^-$  suggest that the extra electron is largely localized. Detachment of such localized electrons induces significant changes to the local bonding environment, resulting in large structural changes. While description of electron delocalization versus localization is still challenging for DFT methods [4,93], available calculations suggest that the  $(TiO_2)_n^-$  ( $n \ge 3$ ) clusters possess a similar undercoordinate Ti site where the extra electron is localized [25,94], as shown in Figure 6 for the  $Ti_3O_6^-$  cluster. The localization of the extra electron in the  $(TiO_2)_n^{-}$  clusters effectively generates a localized Ti<sup>3+</sup> site, thus providing molecular



Figure 6. Electron spin density of the  $Ti_3O_6^-$  cluster anion at the B3LYP level [25].

models equivalent to an F-center defect in bulk TiO<sub>2</sub>. F-centers are common defects in bulk TiO<sub>2</sub>, governing both its catalytic and optical properties [54,55].

4.2.  $(V_2O_5)_n^-$  (n = 2–4): polyhedral cages and electron delocalization versus localization

A series of  $(V_2O_5)_n$  polyhedral cage clusters were predicted using DFT calculations [3]. A subsequent experimental study on  $(V_2O_5)_n$  (*n* = 2–4) using infrared multiple photon dissociation (IRMPD) spectroscopy confirmed the cage structures and revealed a size-dependent delocalization versus localization of the extra electron in the anions [4]. Another IRMPD study further showed that substitution of V by Ti in bimetallic oxide clusters,  $(V_2O_5)_{n-1}(VTiO_5)^-$  (*n* = 2–4), does not change the cage frameworks [5]. The structural robustness of the  $(V_2O_5)_n$  cage clusters makes them ideal molecular models for catalytic investigations [6]. The PES spectra for the three  $M_4O_{10}^-$  (M = V, Nb, Ta) clusters are relatively sharp and broaden slightly going down the periodic table (Figure 2, right column), indicating only minor anion-to-neutral structural changes upon electron detachment. The width of band X for  $(V_2O_5)_n^-$  increases significantly as a function of size (Figure 2, left column), resulting in a reorganization energy of 0.05, 0.20, and 0.61 eV for n = 2-4, respectively. This trend is consistent with a transition from electron delocalization to localization as a function of cluster size, as borne out from the pictures of their singly occupied MOs (SOMOs) (Figure 7).

The observation of the enlarged energy gaps in the  $(V_2O_5)_n^$ clusters relative to bulk  $V_2O_5$  is likely due to the unique polyhedral cage structures (Figure 7), in which each V atom is tetracoordinated with one terminal O atom (V=O) and three bridging O atoms (V-O). This coordination environment differs from the  $V_2O_5$  bulk oxide [95]. It has been reported that supported group VB oxides possess greater band gaps than their corresponding bulk oxides [96], although the exact identity of the surface species is not well understood. In particular, the catalytic activity of supported vanadium oxide catalysts has been shown to correlate with its UV-Vis absorption edge [97], which falls in the same range as the HOMO– LUMO excitation energies of gas-phase  $(V_2O_5)_n$  clusters. These



Figure 7. Optimized ground-state structures of (a) V<sub>4</sub>O<sub>10</sub>, (b) V<sub>6</sub>O<sub>15</sub>, and (c) V<sub>8</sub>O<sub>20</sub>, and the pictures of 3d based singly occupied molecular orbitals of their anions (d-f) [39].

observations suggest that the polyhedral cage clusters may be present on oxide surfaces and play a role in catalysis.

The different energy gaps (Figure 2, left column) suggest that the  $(V_2O_5)_n$  clusters should exhibit size-dependent reactivity. The smaller gap in  $V_4O_{10}$  should render it more reactive, in particular for those reactions involving ligand-to-metal charge transfers, such as H-abstraction reactions,  $V^{5+} = O + HR \rightarrow V^{4+}-OH + R$ . The  $V_4O_{10}^+$ cation was shown recently to be able to abstract a H from CH<sub>4</sub> via a barrierless reaction [6]. Similarly, the periodic trend from 3d to 5d (Figure 2, right column) implies that  $V_4O_{10}$  should be more reactive than its Nb/Ta counterparts.

#### 4.3. Terminal versus bridging oxygen sites: $Nb_3O_2^-$ versus $Ta_3O_2^-$

The coordination of oxygen to a metal center on oxide surfaces occurs in either terminal or bridging fashion, which can be distinguished using Raman and IR techniques [98]. Oxide clusters provide molecular models for the coordination environment on oxide surfaces. In a comparative study of Nb and Ta oxide clusters, we found a unusual  $C_1$  (<sup>1</sup>A) ground-state structure for Nb<sub>3</sub>O<sub>2</sub><sup>-</sup> with a terminal O atom (Figure 8a) [42], in which every Nb atom has a different oxidation state: 0, +1, and +3. The intuitively anticipated dibridged  $C_2$  (<sup>1</sup>A) structure (Figure 8b) is a minimum, but it is 0.53 eV higher in energy. The  $C_1$  (<sup>1</sup>A) ground state of Nb<sub>3</sub>O<sub>2</sub><sup>-</sup> possesses characteristic MOs (Figure 9a-c), which gives rise to unique detachment transitions and are confirmed by the PES spectra [42]. The valent isoelectronic  $Ta_3O_2^-$  cluster, on the other hand, possesses the expected  $C_2$  (<sup>1</sup>A) ground state [43], with the  $C_1$  (<sup>1</sup>A) structure being 0.56 eV above the ground state (Figure 8c). The  $C_2$  (<sup>1</sup>A) ground state of Ta<sub>3</sub>O<sub>2</sub><sup>-</sup> is also confirmed by its PES spectra [43].

The different ground-state structures for  $Nb_3O_2^-$  and  $Ta_3O_2^-$  can be traced to the electronic structure of the monoxide species  $M_3O^-$ (M = Nb, Ta) [42,43]. The HOMO (2b<sub>2</sub>) of  $M_3O^-$  is primarily an



**Figure 8.** (a) Schematic of the unusual Nb<sub>3</sub>O<sub>2</sub><sup>-</sup> ( $C_1$ , <sup>1</sup>A) ground state, (b) its dibridged ( $C_2$ , <sup>1</sup>A) structure, and (c) the energetic relationship of these two structures for Nb<sub>3</sub>O<sub>2</sub><sup>-</sup> versus Ta<sub>3</sub>O<sub>2</sub><sup>-</sup>.



**Figure 9.** Pictures of selected O 2p-derived molecular orbitals for  $Nb_3O_2^-$  [42]. Their calculated vertical detachment energies are shown in parentheses. Note that O 2p orbitals from the terminal O atom (a-c) show substantially lower binding energies than that from the bridging O atom (d).

M 5s/6s  $\sigma$ -antibonding orbital, whereas HOMO-2 (1a<sub>2</sub>) shows primary M 4d/5d  $\pi$ -bonding/antibonding character. The second O atom is expected to interact strongly with either the HOMO or the HOMO-2 of M<sub>3</sub>O<sup>-</sup>, resulting in a terminal or bridging O ligand in  $M_3O_2^-$ , respectively. For M = Nb, the HOMO and HOMO-2 show a sizable orbital energy difference ( $\sim$ 1.4 eV), and thus the second O atom primarily interacts with the HOMO, forming the unusual terminal Nb=O unit. In contrast, a substantially smaller HOMO and HOMO-2 energy gap ( $\sim$ 0.5 eV) is observed for M = Ta. Consequently, its HOMO-2 becomes energetically competitive to interact with the second O atom, resulting in a dibridged ground state for  $Ta_3O_2^-$ . The difference in the energy gap between HOMO (2b<sub>2</sub>) and HOMO-2 (1a<sub>2</sub>) for Nb<sub>3</sub>O<sup>-</sup> versus Ta<sub>3</sub>O<sup>-</sup> may be attributed to the relativistic effects [99] in the Ta anion, whose 6s-based 2b<sub>2</sub> orbital is energetically stabilized (by  $\sim 0.2$  eV relative to Nb<sub>3</sub>O<sup>-</sup>) and the 5d-based  $1a_2$  orbital is destabilized (by ~0.7 eV relative to Nb<sub>3</sub>O<sup>-</sup>).

Terminal Nb=O group is common on Nb oxide surfaces and is suggested to play an important role in the catalytic activities of niobia catalysts [100]. What is surprising is the early appearance of the terminal O atom, considering that  $Nb_3O_2^-$  is metal-rich. Due to their substantially different electron binding energies (Figure 9), the terminal and bridging O atoms in  $Nb_3O_2^-$  should exhibit distinct chemical reactivities, which may be exploited in gas-phase cluster reactions.

#### 4.4. A single W center can stabilize oxygen radicals: $WO_4^-$ and $WO_4$

The PES spectra of WO<sub>4</sub><sup>-</sup> reveal a very high electron binding energy (VDE: 5.44 eV) [26], which suggests that the WO<sub>4</sub> neutral is a strong oxidizer and can be considered as a superhalogen [101]. The structure of the WO<sub>4</sub><sup>-</sup> anion can be understood on the basis of the closed-shell tetrahedral WO<sub>4</sub><sup>2-</sup> dianion, which exists in solids such as Na<sub>2</sub>WO<sub>4</sub>. Removal of an electron from the WO<sub>4</sub><sup>2-</sup> dianion results in a Jahn–Teller unstable WO<sub>4</sub><sup>-</sup> anion, which distorts to a lower symmetry  $C_{2v}$  structure (Figure 10a). The extra electron in WO<sub>4</sub><sup>-</sup> is delocalized over the two oxyl O atoms (Figure 10c), resulting in significant stabilization. The WO<sub>4</sub> neutral possesses a triplet  $D_{2d}$  (<sup>3</sup>A<sub>2</sub>) ground state (Figure 10b), which can be considered as a diradical – a resonance hybrid of two equivalent  $C_{2v}$  structures – with the spin density shared on all four oxygen atoms (Figure 10d). The WO<sub>4</sub><sup>-</sup> and WO<sub>4</sub> clusters demonstrated that oxygen radicals can be stabilized by a single tungsten center. Such radicals may



**Figure 10.** Optimized geometries for (a)  $WO_4^- C_{2v}$  (<sup>2</sup>B<sub>2</sub>) and (b)  $WO_4 D_{2d}$  (<sup>3</sup>A<sub>2</sub>) at the B3LYP level [26], and the valence bond description of (c)  $WO_4^-$  and (d)  $WO_4$ . Bond distances (in Å) and bond angles (°) are shown.



**Figure 11.** Typical mass distribution of the  $W_n O_m^-$  clusters generated in the laser vaporization supersonic cluster source under oxygen-rich conditions.

be present on tungsten oxide surfaces and should be highly reactive chemically.

#### 4.5. Superoxides $(O_2^-)$ versus van der Waals complexes

Figure 11 shows a typical mass distribution of  $W_n O_m^{-}$  clusters under O<sub>2</sub>-rich source conditions. The mass distributions terminate at the stoichiometry  $W_n O_{3n+2}^{-}$  (*n* = 1–3) [34]. This hints an interesting possibility to model the interaction between stoichiometric  $(WO_3)_n^-$  clusters and dioxygen, since the stoichiometry  $W_nO_{3n+2}^$ can be considered as  $(WO_3)_n(O_2^-)$ . Indeed, DFT calculations show that both  $W_2O_8^-$  and  $W_3O_{11}^-$  possess  $C_1$  (<sup>2</sup>A) ground-state structures (Figure 12) [34], which bear considerable resemblance to those of  $W_2O_6^-$  and  $W_3O_9^-$  interacting with an  $O_2$  unit. The calculated O–O bond distance of the O<sub>2</sub> unit is 1.33 Å in both clusters, very similar to that of the free superoxide anion  $O_2^-$  (1.34 Å at the same level), suggesting that the  $W_2O_8^-$  and  $W_3O_{11}^-$  clusters can be viewed as a superoxide  $\mathrm{O_2}^-$  bound to neutral  $\mathrm{W_2O_6}$  and W<sub>3</sub>O<sub>9</sub>, respectively. The superoxide fragment is bound in an asymmetric side-on fashion, with W-O bond distances of 2.06 and 2.27 Å in  $W_2O_8^-$  and 2.06 and 2.26 Å in  $W_3O_{11}^-$  (Figure 12). The optimized structures of W<sub>2</sub>O<sub>8</sub> and W<sub>3</sub>O<sub>11</sub> neutrals are dramatically different. A large increase in the separation between the O<sub>2</sub> fragment and the tungsten site is revealed, with the calculated W-O distances increasing to 2.67 and 3.49 Å in neutral W<sub>2</sub>O<sub>8</sub> and to 3.83 and 4.57 Å in  $W_3O_{11}$ . In addition, the O–O distance of the  $O_2$ unit is reduced from 1.33 Å in the anions to 1.20 Å in the neutrals, very close to that of free  $O_2$  (1.21 Å at the same level).

Thus, a single 5d electron in the  $W_2O_6^-$  and  $W_3O_9^-$  anions provides the primary driving force to activate  $O_2$ , resulting in superoxide  $W_2O_8^-$  and  $W_3O_{11}^-$  complexes (via charge transfer) [102–110]. The adsorption energies are evaluated:  $W_2O_6^- + O_2 \rightarrow W_2O_8^-$  (-1.24 eV) and  $W_3O_9^- + O_2 \rightarrow W_3O_{11}^-$  (-1.42 eV). In contrast, the



Figure 12. Calculated ground-state structures at the B3LYP level for (a)  $W_2O_6^-$ , (b)  $W_3O_9^-$ , (c)  $W_2O_8^-$ , and (d)  $W_3O_{11}^-$  [34].

stoichiometric neutral W<sub>2</sub>O<sub>6</sub> and W<sub>3</sub>O<sub>9</sub> clusters show extremely weak interactions with O<sub>2</sub> (calculated as < 0.1 eV in both cases), essentially forming only physisorbed W<sub>2</sub>O<sub>6</sub>(O<sub>2</sub>) and W<sub>3</sub>O<sub>9</sub>(O<sub>2</sub>) van der Waals complexes. The observed photodetachment thresholds of W<sub>2</sub>O<sub>8</sub><sup>-</sup> and W<sub>3</sub>O<sub>11</sub><sup>-</sup> are extremely high, which are estimated to be ~6.4 and ~6.9 eV, respectively, consistent with electronic transitions from O 2p derived MOs. For comparison, the ground-state VDEs for W<sub>2</sub>O<sub>6</sub><sup>-</sup> and W<sub>3</sub>O<sub>9</sub><sup>-</sup> (Figure 13) are 3.63 and ~4.2 eV, respectively [28,29].

#### 4.6. From gas phase to model oxide surfaces: the W<sub>3</sub>O<sub>9</sub> cluster

The electronic structure of neutral W<sub>3</sub>O<sub>9</sub> cluster is probed from its anion PES (Figure 13) [29], yielding the neutral ground and excited states (X and A). These electronic states are separated by an energy gap of  $\sim$ 3.3 eV, which is close to the band gap of bulk WO<sub>3</sub> (indirect gap:  $\sim$ 2.6 eV; direct gap:  $\sim$ 3.5–3.7 eV) [111]. The  $W_3O_9$  cluster is found to possess a  $D_{3h}$  (<sup>1</sup>A'<sub>1</sub>) ground state [29], which possesses three bridging and six terminal oxygen atoms. Each W<sup>6+</sup> center in W<sub>3</sub>O<sub>9</sub> is thus tetracoordinated by two W–O bonds and two W=O bonds, forming a robust circular cluster. It turns out that nearly monodispersed W<sub>3</sub>O<sub>9</sub> clusters can be produced by direct sublimation of a bulk WO<sub>3</sub> sample and deposited on a  $TiO_2(110)$  surface [35]. The supported  $W_3O_9$  clusters are found to keep the gas phase cyclic structures, demonstrating the stability and robustness of the W<sub>3</sub>O<sub>9</sub> cluster. The W<sub>3</sub>O<sub>9</sub> clusters provide an ideal model system for reactivity studies and have been shown to be an efficient catalyst for dehydration of alcohols [112,113], even though DFT calculations have revealed that there are significant cluster-surface interactions [113,114].



**Figure 13.** Photoelectron spectrum of  $W_3O_9^-$  at 157 nm [34].



**Figure 14.** Pictures of (a) the singly occupied molecular orbital of  $W_3O_9^-$  and (b) the highest occupied molecular orbital of  $W_3O_9^{-2}$  [29].

#### 5. Delocalized d orbital bonding in metal-rich oxide clusters

The concept of aromaticity was introduced in organic chemistry to describe delocalized  $\pi$ -bonding in planar, cyclic, and conjugate molecules that possess (4n + 2)  $\pi$ -electrons. It has very recently been advanced into all-metal clusters [58,63,64]. Transition metal atoms can form  $\delta$  bond [115–117] in addition to  $\sigma$  and  $\pi$  bonds. Thus, while main group molecules give rise to  $\sigma$ - and  $\pi$ -aromaticity, transition metal species offer new opportunities to explore dorbital aromaticity and  $\delta$ -aromaticity [40]. Metal-rich early transition metal oxide clusters provide a fertile ground to explore these new types of chemical bonding.

## 5.1. d-Orbital aromaticity

The first experimental and theoretical evidence of d-orbital aromaticity [29] was revealed in 4d and 5d oxide clusters:  $M_3O_9^-$  and  $M_3O_9^{-2-}$  (M = W, Mo). The ground-state structures and HOMO of  $W_3O_9^{--}$  and  $W_3O_9^{-2-}$  are shown in Figure 14. The  $W_3O_9^{--}$  anion and W<sub>3</sub>O<sub>9</sub><sup>2-</sup> dianion possess one and two W 5d electrons, respectively. In W<sub>3</sub>O<sub>9</sub><sup>-</sup>, the SOMO (Figure 14a) depicts nearly pure threecenter W–W  $\sigma$  bonding interactions with very little contribution from the O atoms, that is, a strong three-center one-electron (3c-1e) W–W bond. Addition of a second electron to the a' SOMO gives rise to a closed-shell  $W_3 O_9^{2-}$  dianion, which also possesses  $D_{3h}$ symmetry and a three-center two-electron (3c-2e) bond (Figure 14b). Surprisingly, despite the strong intramolecular coulomb repulsion, the  $W_3 O_9^{2-}$  dianion is predicted to be a stable gas-phase species with a calculated electron binding energy of 0.03 eV relative to  $W_3O_9^-$  (at the B3LYP level). More significantly, the second electron is shown to induce a considerable shortening of the W-W bond distance (by 0.19 Å). The calculated nucleus independent chemical shift (NICS) [118] at the ring center amounts to -12.8 for  $W_3O_9^-$  and -21.5 for  $W_3O_9^{2-}$ , suggesting that the  $W_3O_9^-$  and  $W_3 O_9^{2-}$  clusters are indeed highly aromatic.

#### 5.2. $\delta$ -Aromaticity: a new mode of chemical bonding

δ-Aromaticity was recently observed for the first time in the Ta<sub>3</sub>O<sub>3</sub><sup>-</sup> cluster [38]. The PES spectra of Ta<sub>3</sub>O<sub>3</sub><sup>-</sup> are shown in Figure 15a. Three well-resolved bands (*X*, *A*, and *B*) are observed at the lower binding energy side. The *X* band is much more intense and shows a discernible splitting at 193 nm. The ground-state structure of Ta<sub>3</sub>O<sub>3</sub><sup>-</sup> is found to be  $D_{3h}$  (<sup>1</sup>A<sub>1</sub>). MO analysis shows that out of the 34 valence electrons in Ta<sub>3</sub>O<sub>3</sub><sup>-</sup>, 24 belong to either pure oxygen lone pairs or are responsible for the Ta–O bonding. The remaining 10 valence electrons are responsible for direct Ta–Ta bonding, as shown in Figure 15b. Among these five MOs, three (the partially bonding/antibonding degenerate 4e' HOMO and the bonding 3a'<sub>1</sub> HOMO–3) are responsible for σ-bonding of the triangular Ta<sub>3</sub> framework. The HOMO–2 (2a''<sub>2</sub>) is a bonding  $\pi$  orbital composed primarily of Ta 5d orbitals, which gives rise to  $\pi$ -aromaticity according to the (4*n* + 2) Hückel rule.

The most interesting MO is HOMO–1 (4a'<sub>1</sub>), a completely bonding orbital mainly coming from the overlap of the  $d_{z^2}$  orbital on each Ta atom. This is a  $\delta$  MO, because it possesses two nodal surfaces perpendicular to the  $C_3$  axis. Analogous to the circularly delocalized  $\pi$ -MO over the three carbon atoms in  $C_3H_3^+$ , which renders  $C_3H_3^+ \pi$ -aromatic, the circular delocalization of the  $4a'_1$  MO gives rise to  $\delta$ -aromaticity in Ta<sub>3</sub>O<sub>3</sub><sup>-</sup>, which is also consistent with the (4n + 2) Hückel rule. The  $\delta$ -aromaticity found in this cluster is a new mode of chemical bonding, which can only occur in multicenter transition metal systems. Similar  $\delta$ -aromaticity may exist in many cyclic systems containing the transition metal atoms in low oxidation states [119,120].



**Figure 15.** (a) Photoelectron spectra of  $Ta_3O_3^-$  at 193 and 157 nm and (b) the five valence molecular orbitals that are responsible for Ta–Ta bonding in the  $Ta_3O_3^-D_{3h}(^1A'_1)$  ground state [38].

5.3. Evidence for resonance stabilization of  $\delta$  orbitals in the  $Ta_3O_3^-$  cluster

A study of the Ta<sub>3</sub>O<sub>n</sub><sup>-</sup> (n = 0-8) series of clusters provides a systematic understanding of their structural evolution and sequential oxidation [43,120], allowing the  $\delta$  orbital to be followed as a function of O content. A  $\delta$ -type MO can be identified in the Ta<sub>3</sub>O<sub>n</sub><sup>-</sup> (n = 0-5) clusters, along with the specific experimental PES band associated with it, as shown in Figure 16. Depending on the geometric shape and the O atom coordination environment in a Ta<sub>3</sub>O<sub>n</sub><sup>-</sup> cluster, the  $\delta$  orbital is found to be primarily localized on a single Ta center in Ta<sub>3</sub>O<sub>5</sub><sup>-</sup>, shared by two Ta centers in Ta<sub>3</sub>O<sub>4</sub><sup>-</sup>,



**Figure 16.** Experimental (solid line) and computational (dashed line) vertical detachment energies from the  $\delta$  orbital in Ta<sub>3</sub>O<sub>n</sub><sup>-</sup> (*n* = 1–5) as a function of O content.

partially delocalized over three Ta centers but distorted in Ta<sub>3</sub>O<sup>-</sup> and Ta<sub>3</sub>O<sub>2</sub><sup>-</sup>, and completely delocalized over three Ta centers in Ta<sub>3</sub><sup>-</sup> and Ta<sub>3</sub>O<sub>3</sub><sup>-</sup>. Although  $\delta$  bonding is substantially weaker than  $\sigma$  and  $\pi$  bonding [117], there is observable stabilization effect due to the delocalization of the  $\delta$  orbital. For example, the VDE of the  $\delta$ orbital in Ta<sub>3</sub>O<sub>3</sub><sup>-</sup> is the highest because this MO is highly delocalized in the D<sub>3h</sub> cluster.

## 6. Concluding remarks

In conclusion, anion photoelectron spectroscopy is employed in combination with density-functional theory calculations to probe the intrinsic electronic and structural properties of early transition metal oxide clusters and to provide well-defined and controllable cluster models towards mechanistic insights into oxide surfaces and catalysis. Selected cluster systems are discussed in this frontiers article. The energy gap evolution as a function of size is probed in the stoichiometric  $(TiO_2)_n^-$ ,  $(V_2O_5)_n^-$ , and  $(CrO_3)_n^-$  clusters, and each system is shown to approach the band gap of bulk oxides differently. Photoelectron spectroscopy is shown to be a sensitive technique to probe the nature of localization versus delocalization of the extra d electron. The d electron in  $(TiO_2)_n^-$  is largely localized and that in  $(CrO_3)_n^-$  is delocalized, whereas the extra d electron in the  $(V_2O_5)_n^-$  polyhedral cage clusters undergoes a size-dependent transition from delocalization to localization. The localized 3d electron in  $(TiO_2)_n^-$  generates  $Ti^{3+}$  centers, which are common defects in bulk TiO<sub>2</sub>. The enlarged energy gap in the  $(V_2O_5)_n^-$  clusters relative to bulk oxide correlates well with the absorption edge on catalytic V<sub>2</sub>O<sub>5</sub> surfaces, suggesting that the polyhedral cage  $(V_2O_5)_n$  clusters may exist on oxide surfaces. A variety of other model clusters are also discussed, such as the oxygen radical or diradical on a single W<sup>6+</sup> site, the superoxide  $(WO_3)_n(O_2^{-})$  complexes for dioxygen activation, the van der Waals  $(WO_3)_n(O_2)$  complexes, and terminal versus bridging oxygen in  $M_3O_2^-$  (M = Nb, Ta) clusters. Also highlighted is the  $W_3O_9$  cluster, which is a stable cyclic cluster in the gas phase and has been successfully deposited on a model oxide surface. Finally, delocalized multicenter d–d bonding in metal-rich oxide clusters is explored. Both d-orbital aromaticity and  $\delta$ -aromaticity have been observed in early transition metal oxide clusters containing low oxidation-state metal centers.

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194

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