

# On the Structure and Chemical Bonding of Tri-Tungsten Oxide Clusters $W_3O_n^-$ and $W_3O_n$ ( $n = 7-10$ ): $W_3O_8$ As A Potential Molecular Model for O-Deficient Defect Sites in Tungsten Oxides

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Electronic and structural properties of a series of tri-tungsten oxide clusters,  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7-10$ ), are investigated using photoelectron spectroscopy and density functional theory (DFT) calculations. Both W 5d and O 2p detachment features are observed for  $n = 7-9$ , whereas only detachment features from O 2p-type orbitals are observed for  $W_3O_{10}^-$  at high electron binding energies ( $>7$  eV). A large energy gap ( $\sim 3.4$  eV) is observed for the stoichiometric  $W_3O_9$  cluster, which already reaches the bulk value, suggesting that  $W_3O_9$  can be viewed as the smallest molecular model for bulk  $WO_3$ . DFT calculations are carried out to locate the most stable structures for both the anion and neutral clusters; time-dependent DFT method is used to predict the vertical detachment energies and to compare with the experimental data. It is shown that  $W_3O_9$  possesses a  $D_{3h}$  structure, in which each W atom is tetrahedrally coordinated with two bridging O atoms and two terminal O atoms.  $W_3O_8$  and  $W_3O_7$  can be viewed as removing one and two terminal O atoms from  $W_3O_9$ , respectively, whereas  $W_3O_{10}$  can be viewed as replacing a terminal O in  $W_3O_9$  by a peroxo  $O_2$  unit. We show that  $W_3O_8$  contains a localized  $W^{4+}$  site, which can readily react with  $O_2$  to form the  $W_3O_{10}$  clusters with a calculated  $O_2$  adsorption energy of  $-78$  kcal/mol. It is suggested that the  $W_3O_8$  cluster can be viewed as a molecular model for O-deficient site in tungsten oxides.

## 1. Introduction

Tungsten oxides have many industrial applications<sup>1-4</sup> and are important acid-base and redox catalysts.<sup>5-11</sup> However, the identification of active sites in metal oxide catalysts has been very difficult. Gas-phase cluster studies have been considered as an alternative approach to obtain fundamental insight into the complicated structures and chemical processes in oxide materials and catalysts.<sup>12-21</sup> Interest in transition-metal oxide clusters has been motivated in particular by the use of these species to aid the elucidation of the mechanisms of catalytic reactions.<sup>22,23</sup> Gas-phase studies, coupled with state-of-the-art theoretical calculations, can provide molecular level insight into the nature of active species in catalysis.<sup>13,14</sup> As a first step in developing a comprehensive understanding of complex catalytic processes on early transition-metal oxides, we are interested in systematic studies of the electronic structure and chemical bonding of size-selected tungsten oxide clusters. Recently, we have reported joint experimental and theoretical investigations on a variety of tungsten oxide clusters.<sup>21,24,25</sup> To mimic the geometric and electronic properties of tungsten oxide surfaces and defects, relatively large  $W_mO_n$  clusters are of interest. In the present work, we investigate the electronic structure and chemical bonding of the tri-tungsten oxide clusters,  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7-10$ ), which include the stoichiometric  $W_3O_9$  cluster and both O-deficient ( $W_3O_7$  and  $W_3O_8$ ) and O-rich ( $W_3O_{10}$ ) clusters.

There have been relatively few reports on tri-tungsten oxide clusters,<sup>26-28</sup> and very little is known about tri-tungsten oxide species, except  $W_3O_9$ . Early mass-spectrometric studies<sup>26,27</sup> indicated that the vapor of tungsten trioxide consists mainly of the stoichiometric molecule  $W_3O_9$ . Weltner et al.<sup>28</sup> performed a matrix infrared spectroscopic study on tungsten oxide clusters and tentatively assigned certain infrared bands to  $W_3O_8/W_3O_9$  on the basis of their intensity variations with vaporization conditions. Sun et al.<sup>29</sup> recently reported the photoelectron spectrum of  $W_3O_9^-$  at 193 nm together with other stoichiometric  $W_nO_{3n}^-$  ( $n = 1, 2, 4$ ) clusters. They also presented the optimized structures of  $W_3O_9$  and  $W_3O_9^-$  at the BPW91 level.

We have obtained photoelectron spectra of  $W_3O_n^-$  ( $n = 7-10$ ) at 157 nm (7.866 eV). The high photon energy is necessary because of the relatively high electron binding energies of the oxide cluster anions, in particular, the O-rich species. A large energy gap was observed for  $W_3O_9^-$ , consistent with a stable stoichiometric  $W_3O_9$  molecule, in which W reaches its highest oxidation state ( $W^{6+}$ ). Lower binding energy features due to excess 5d electrons were observed for the O-deficient clusters, whereas high electron binding energies were observed for the O-rich  $W_3O_{10}^-$  cluster. Extensive density functional theory (DFT) calculations were performed to elucidate the structures and bonding in the tri-tungsten oxide clusters in both the neutral and anionic species,  $W_3O_n$  and  $W_3O_n^-$  ( $n = 7-10$ ). In particular, the ground state of  $W_3O_8$  is found to be an interesting species, which may be viewed as a model for O-deficient defect sites. The ground state of  $W_3O_{10}$  is found to be a peroxo complex, which can be viewed to be formed from

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chemisorption of O<sub>2</sub> on W<sub>3</sub>O<sub>8</sub> and may serve as important intermediate in catalytic oxidation reactions.

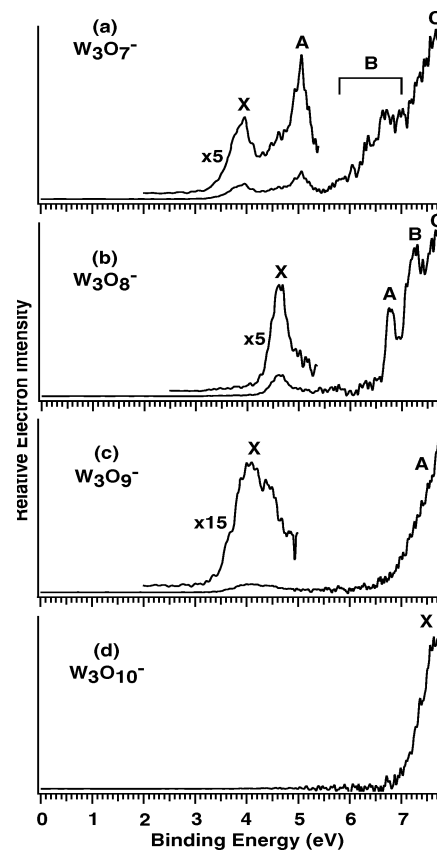
## 2. Experimental and Theoretical Methods

**2.1. Photoelectron Spectroscopy.** The experiments were carried out using a magnetic-bottle photoelectron spectroscopy (PES) apparatus equipped with a laser vaporization supersonic cluster source.<sup>30,31</sup> Briefly, W<sub>m</sub>O<sub>n</sub><sup>-</sup> cluster anions were produced by laser vaporization of a pure tungsten target in the presence of helium carrier gas seeded with 0.5% O<sub>2</sub> and were analyzed using a time-of-flight mass spectrometer. The W<sub>3</sub>O<sub>n</sub><sup>-</sup> (*n* = 7–10) clusters of current interest were each mass selected and decelerated before being photodetached with 157-nm photons from an F<sub>2</sub> excimer laser. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. Photoelectron spectra were calibrated using the known spectrum of Rh<sup>-</sup>, and the energy resolution of the apparatus was  $\Delta E_k/E_k \approx 2.5\%$ , that is,  $\sim 25$  meV for 1 eV electrons.

**2.2. Density Functional Calculations.** The theoretical calculations were performed at the DFT level using the B3LYP hybrid functional.<sup>32–34</sup> A number of structural candidates were evaluated, and the search for the global minima was performed using analytical gradients with the Stuttgart 14-valence-electron pseudopotentials and the valence basis sets<sup>35,36</sup> augmented with two f-type and one g-type polarization functions [ $\zeta(f) = 0.256$ ,  $0.825$ ;  $\zeta(g) = 0.627$ ] for tungsten as recommended by Martin and Sundermann<sup>37</sup> and the aug-cc-pVTZ basis set for oxygen.<sup>38,39</sup> Scalar relativistic effects, i.e., the mass-velocity and Darwin effects, were taken into account via the quasirelativistic pseudopotentials. Since we were mainly interested in explaining the experimentally observed PES spectra, no further effort was devoted to resolve the spin–orbit coupled fine structures in the calculated spectra. Our previous results on tungsten oxides showed that spin–orbit coupling effects would shift the orbital energies by up to a few tenth of an eV, which would not affect the spectral assignment.<sup>40</sup> Only a selected set of optimized structures (the ground state and a few low-lying isomers), considered to be important in interpreting the experimental data, are reported. Vibrational frequency calculations were performed at the same level of theory to verify the nature of the stationary points. The vertical detachment energies (VDEs) were calculated using a combined  $\Delta$ SCF-TDDFT approach, as we previously outlined.<sup>41,42</sup> In this approach, the ground-state energies of the anions and the neutrals were calculated from the  $\Delta$ SCF energy difference at the B3LYP level, whereas the excited states of the one-electron-detached species were obtained from TDDFT calculations of the neutrals. For all calculations, the extra fine integration grid was used to obtain highly accurate DFT results. All calculations were accomplished using the NWChem 4.6 program and the Molecular Science Computing Facility located at the Environmental Molecular Sciences Laboratory.<sup>43</sup> The Extensible Computational Chemistry Environment software was used to generate the three-dimensional contours of the calculated Kohn–Sham orbitals.<sup>44</sup>

## 3. Experimental Results

The PES spectra of W<sub>3</sub>O<sub>n</sub><sup>-</sup> (*n* = 7–10) measured at 157 nm are shown in Figure 1. The observed spectral bands are labeled with letters (X, A, B, C). The low binding energy features in W<sub>3</sub>O<sub>n</sub><sup>-</sup> (*n* = 7–9) are expanded to illustrate the spectral details. The obtained VDEs and ground-state adiabatic detachment energies (ADEs) are given in Table 1.



**Figure 1.** Photoelectron spectra of W<sub>3</sub>O<sub>n</sub><sup>-</sup> (*n* = 7–10) at 157 nm (7.866 eV).

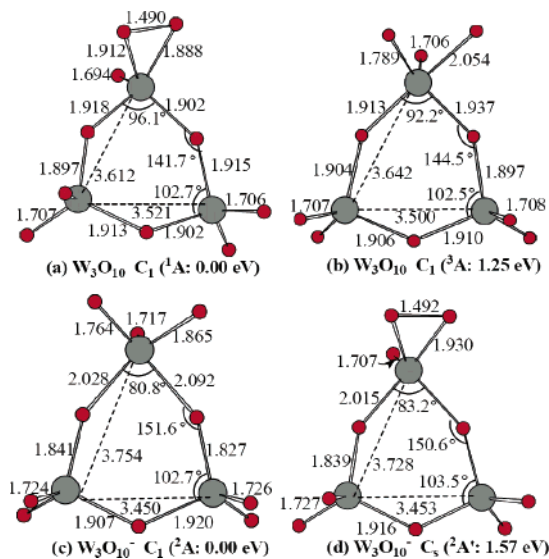
The spectrum of W<sub>3</sub>O<sub>7</sub><sup>-</sup> (Figure 1a) shows two relatively weak bands (X and A) at low binding energies. More intense signals above 6 eV appear to be congested and continuous. The ground-state band X has a VDE of 3.9 eV with a long tail down to  $\sim 3.3$  eV either due to vibrational hot bands or a large geometry change between the anion and neutral ground states. The ADE of the X band was estimated to be  $3.5 \pm 0.1$  eV, which defines the electron affinity (EA) of neutral W<sub>3</sub>O<sub>7</sub>. The large uncertainty was a result of the low energy tail, which made it difficult to define the ADE. Band A with a VDE of 5.04 eV is relatively sharp, which should correspond to the first excited state of W<sub>3</sub>O<sub>7</sub>. A shoulder seems to be present at the lower binding energy side of band A. The spectrum beyond  $\sim 6.0$  eV is featureless, which is labeled with B and C simply to denote two spectral regions.

The spectrum of W<sub>3</sub>O<sub>8</sub><sup>-</sup> (Figure 1b) displays relatively sharp features. A weak band X with a VDE of 4.62 eV is followed by a large energy gap and three well-defined spectral features (A, B, C) at high binding energies. The ground-state band X yields an ADE of 4.37 eV, which defines the EA of neutral W<sub>3</sub>O<sub>8</sub>. The first excited-state band (A) at a VDE of 6.78 eV gives a X–A gap of 2.16 eV. The VDEs of bands B and C are measured to be 7.23 and 7.65 eV, respectively.

The PES spectrum of the stoichiometric W<sub>3</sub>O<sub>9</sub><sup>-</sup> cluster is shown in Figure 1c. The ground-state X has weak intensity and is very broad, suggesting a large geometry change between the anion and neutral ground state. The X band yields a VDE of 4.2 eV and an ADE of 3.55 eV. The X band is followed by a large energy gap and the first excited-state band (A) is located at a high binding energy with an estimated onset of  $\sim 7$  eV. No distinct features were observed in the higher binding energy







**Figure 5.** Optimized structures and their relative energies for  $W_3O_{10}$  and  $W_3O_{10}^-$ . The bond lengths are in angstroms and bond angles in degrees.

converged to the same structure. The ground state of  $W_3O_9$  was found to be closed shell with  $D_{3h}$  ( ${}^1A_1'$ ) symmetry. Each tungsten atom is tetrahedrally coordinated with two terminal and two bridging O atoms (Figure 2a). This is basically consistent with that identified by Sun et al.<sup>29</sup> at BPW91, except that the structure of Sun et al. possesses lower symmetry ( $C_{3v}$ ). The  $W-O_t$  and  $W-O_b$  bond lengths are 1.706 and 1.908 Å, close to those expected for  $W=O$  double and  $W-O$  single bonds, respectively. The  $\angle WO_bW$  bond angle is  $137.1^\circ$ , much larger than the  $\angle O_bWO_b$  angle of  $102.9^\circ$ .

The ground state of  $W_3O_9^-$  was found to be a doublet with  $D_{3h}$  ( ${}^2A_1'$ ) symmetry (Figure 2b), similar to that for the neutral. The  $W-O_t$  and  $W-O_b$  bond lengths are 1.724 and 1.923 Å, respectively, only slightly longer than those in the neutral species. However, the  $\angle WO_bW$  and  $\angle O_bWO_b$  bond angles change significantly. The  $\angle WO_bW$  bond angle is  $116.2^\circ$ , decreased by about  $21^\circ$  relative to that of neutral  $W_3O_9$ , whereas the  $\angle O_bWO_b$  bond angle increases by about  $21^\circ$ , so that the  $W_3O_3$  ring is almost a perfect hexagon.<sup>25</sup> This large geometry change between the anion and neutral ground state is consistent with the broad ground-state band observed in the photoelectron spectrum of  $W_3O_9^-$  (Figure 1c). It should be mentioned that there are other low-lying isomers for  $W_3O_9^-$  that are close in energy to the  $D_{3h}$  structure at the DFT level. Further theoretical calculations with more sophisticated methods may be necessary to resolve the true ground state of  $W_3O_9^-$ .

**4.2. Oxygen-Deficient Cluster:  $W_3O_8$  and  $W_3O_8^-$ .** We started the structural searches for the O-deficient clusters by removing O atoms from the ground state of the stoichiometric  $W_3O_9$  cluster. We located two isomers for neutral  $W_3O_8$ . The ground state of  $W_3O_8$  was found to be closed shell with  $C_s$  ( ${}^1A'$ ) symmetry (Figure 3a), which can be viewed as removing one terminal O atom from the  $D_{3h}$   $W_3O_9$ . The other isomer with  $C_{2v}$  ( ${}^1A_1$ ) symmetry (Figure 3b) is 0.46 eV higher in energy and is derived from removing one bridging O atom from  $W_3O_9$ . In the anion, the  $C_{2v}$  structure (Figure 3c) was found to be the ground state, becoming more stable than the  $C_s$  isomer (Figure 3d) by 0.12 eV. The structures of the two  $W_3O_8^-$  isomers are very similar to their corresponding neutrals with very little geometrical changes, consistent with the relatively sharp PES features observed for  $W_3O_8^-$  (Figure 1b).

**4.3. Oxygen-Deficient Cluster:  $W_3O_7$  and  $W_3O_7^-$ .** We performed an extensive search of the potential energy surfaces of  $W_3O_7$  and  $W_3O_7^-$  using the two isomers of  $W_3O_8$  and  $W_3O_8^-$  (Figure 3) as our starting points. We were able to locate four low-lying isomers, as shown in Figure 4. The ground state of neutral  $W_3O_7$  is  $C_s$  ( ${}^1A'$ ) (Figure 4a), which is formed from removing two terminal O atoms on two different W sites from the neutral  $W_3O_9$ . The second low-lying isomer (Figure 4b) also with  $C_s$  symmetry is only 0.08 eV higher in energy and is originated from removing one terminal and one bridging O atom from two different W sites of  $W_3O_9$ . The third isomer of  $W_3O_7$  (Figure 4c), 0.64 eV higher in energy, is formed by removing one terminal and one bridging O atom from the same W atom of  $W_3O_9$ . The  $W_3O_7$  isomer formed by removing two bridging O atoms from  $W_3O_9$  is much higher in energy by 1.47 eV (Figure 4d).

For the  $W_3O_7^-$  anion, the ground state is the dibridged  $C_s$  ( ${}^2A'$ ) structure (Figure 4e), corresponding to the second low-lying isomer of the neutral cluster. The second isomer of  $W_3O_7^-$ , only 0.10 eV higher in energy, corresponds to the ground state of the neutral. The third (Figure 4g) and fourth (Figure 4h) isomers of the anion are similar to the corresponding neutral isomers and are higher in energy by 0.45 and 0.52 eV above the ground state, respectively.

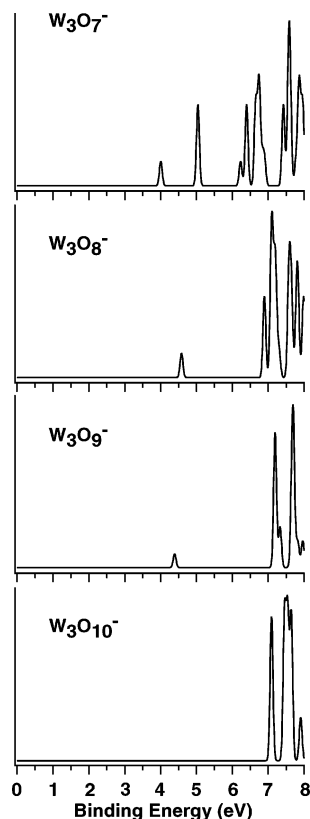
**4.4. Oxygen-Rich Clusters:  $W_3O_{10}$  and  $W_3O_{10}^-$ .** We found two isomers each for  $W_3O_{10}$  and  $W_3O_{10}^-$ , as shown in Figure 5. The ground state of  $W_3O_{10}$  possesses  $C_1$  ( ${}^1A$ ) symmetry (Figure 5a) and can be viewed as replacing a terminal O atom in  $W_3O_9$  by an  $O_2$  unit. A triplet isomer without the  $O_2$  unit is 1.25 eV higher in energy (Figure 5b). This isomer, however, becomes the ground state for the  $W_3O_{10}^-$  anion (Figure 5c), whereas the isomer with the  $O_2$  unit is significantly higher by 1.57 eV in the anion (Figure 5d).

## 5. Discussion

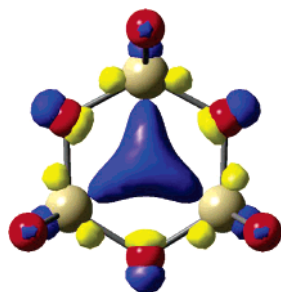
**5.1. Comparisons between Experimental and Theoretical Results and Interpretation of the Photoelectron Spectra.** Photodetachment involves removal of electrons from occupied molecular orbitals (MOs) of the anions. The final states of the electron detachment are the electronic ground and excited states of the corresponding neutrals. The differences between the higher-binding energy bands and the lowest-binding energy band in an anion photoelectron spectrum represent the excitation energies of the neutral cluster. The simulated spectra of the whole  $W_3O_n^-$  ( $n = 7-10$ ) series are shown in Figure 6. All the calculated VDEs are given in Table 1 along with the experimental data.

Within the one-electron formalism, each occupied MO for a closed-shell anion will generate a single PES band with the associated vibrational structures governed by the Franck-Condon principle. However, all the  $W_3O_n^-$  anions are open shell with a single unpaired electron in their lowest energy structures. In these cases, detachment from a fully occupied MO would result in two detachment channels due to the removal of either the spin-down ( $\beta$ ) or the spin-up ( $\alpha$ ) electrons, giving rise to triplet (T) and singlet (S) final states, respectively, as given in Table 1.

**5.1.1.  $W_3O_9^-$ .** The valence electron configuration of  $W_3O_9$  ( ${}^1A_1'$ ,  $D_{3h}$ ) is  $(6e'')^4(12e')^4(7e'')^4(6a_2'')^2$ , all of which are primarily O 2p-based orbitals. In  $W_3O_9^-$  the extra electron enters the  $10a_1'$  LUMO of  $W_3O_9$ , resulting in a doublet ( ${}^2A_1'$ ) state for the anion. The calculated spin densities indicate that the extra electron is equally shared by the three W atoms. The three-dimensional contour of the  $10a_1'$  MO is shown in Figure 7,



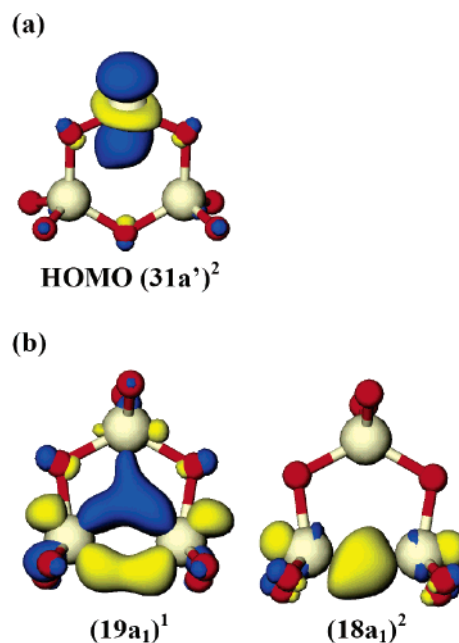
**Figure 6.** Simulated photoelectron spectra of  $W_3O_n^-$  ( $n = 7-10$ ). The simulated spectra were based on the optimized anion ground-state structures (Figures 2–5) and were constructed by fitting the distribution of the calculated vertical detachment energies (Table 1) with unit-area Gaussian functions of 0.04 eV full width at half maximum.



**Figure 7.** The HOMO picture of  $W_3O_9^-$ .

which is a one-electron three-center metal–metal bond.<sup>25</sup> This bond pulls the three W atoms closer in the anion, resulting in a nearly perfect  $W_3O_3$  hexagon in  $W_3O_9^-$  (Figure 2). The broad PES band for the ground-state transition (X, Figure 1c) is in excellent agreement with the large geometry changes upon detachment of the  $10a_1'$  electron in  $W_3O_9^-$ . The calculated VDE of 4.39 eV (Table 1) for this detachment channel compares well with the experimental VDE at  $\sim 4.2$  eV. As shown in Table 1, the calculated VDE for detachment from the first primarily O 2p-type MO,  $6a_2''$  (corresponding to the HOMO of neutral  $W_3O_9$ ), is 7.18 eV, followed immediately by the detachment from the doubly degenerate  $7e''$  MO with a calculated VDE of 7.20 eV. A total of 8 detachment channels are calculated up to 7.8 eV for the O 2p-type orbitals (Table 1). This high density of electronic states from the O 2p-type MOs and their calculated VDEs are in good agreement with the continuous spectral features observed in the high binding energy part of the photoelectron spectrum (Figure 1c).

**5.1.2.  $W_3O_8^-$ .** The ground state of  $W_3O_8$  is the tribridged  $C_s$  structure (Figure 3a), with the dibridged  $C_{2v}$  structure (Figure

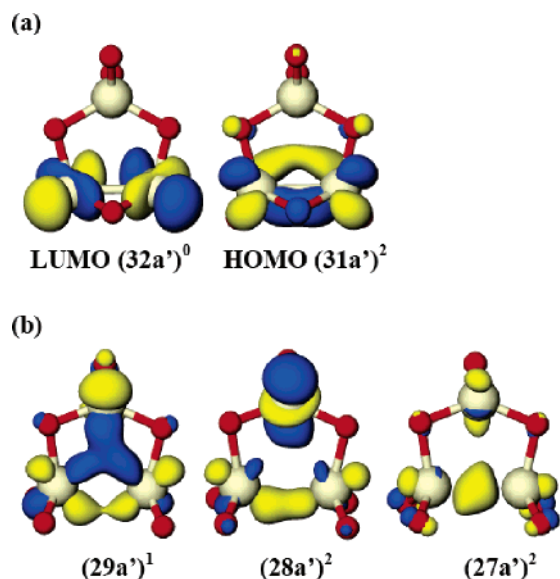


**Figure 8.** (a) The HOMO picture for the ground state of  $W_3O_8$  (Figure 3a). (b) The top two molecular orbitals of the  $W_3O_8^-$  anion (Figure 3c).

3b) being 0.46 eV higher in energy. There is a competition between W–W and W–O bonding. In the  $C_s$  structure, there is no W–W bonding, and the extra pair of d electrons is essentially a lone pair localized on the tricoordinated W atom, as shown in Figure 8a. On the other hand, there is a direct W–W bond in the  $C_{2v}$  structure, which becomes the ground state in the anion (Figure 3c) with a valence-electron configuration of  $(6a_2)^2(14b_2)^2(11b_1)^2(12b_1)^2(7a_2)^2(18a_1)^2(19a_1)^1$ , where the extra electron enters the  $19a_1$  orbital with d–d  $\pi$ -bonding character (Figure 8b). The  $18a_1$  MO is a d–d  $\sigma$ -bonding orbital (Figure 8b), and all MOs from  $7a_2$  and below are of O 2p character.

Photodetachment from the singly occupied  $19a_1$  orbital of  $W_3O_8^-$  yields the first PES band X (VDE: 4.62 eV), which is in excellent agreement with the calculated VDE of 4.58 eV (Table 1). The next detachment channel is from  $18a_1(\beta)$  with a calculated VDE of 6.89 eV, in excellent agreement with band A (VDE = 6.78 eV) (Figure 1b). The calculated VDE from  $18a_1(\alpha)$  is 7.59 eV, which falls in the spectral region where detachments from O 2p-based MOs dominate (Table 1). As shown in Table 1, band B in the photoelectron spectrum can be assigned to electron detachment transitions from the MO group ( $7a_2$ ,  $12b_1$ ,  $11b_1$ ). The calculated VDEs for detachment from  $14b_2(\beta)$  and  $6a_2(\beta)$  are 7.58 and 7.64 eV, respectively, in good agreement with band C (VDE: 7.65 eV). Overall the calculated VDEs from the  $W_3O_8^-$  anion ground state are in excellent agreement with the observed PES spectra. We should point out that the calculated VDEs for the tri-bridged  $C_s$  isomer of  $W_3O_8^-$  are much lower and disagree with the observed photoelectron spectral features.

**5.1.3.  $W_3O_7^-$ .** The  $W_3O_7$  and  $W_3O_7^-$  species represent the most complicated systems in our current study, primarily because of competitions between the W–W, W–O, and W=O bonding. The two low-lying structures of  $W_3O_7$  (Figure 4a, b) have very different W–O connectivities, but surprisingly they are nearly degenerate in energy, with the tribridged structure (Figure 4a) being slightly more stable. Molecular orbital analysis shows that the ground state of  $W_3O_7$  involves  $\pi$ -bonding and antibonding interactions in its HOMO and LUMO, respectively, as shown in Figure 9a.

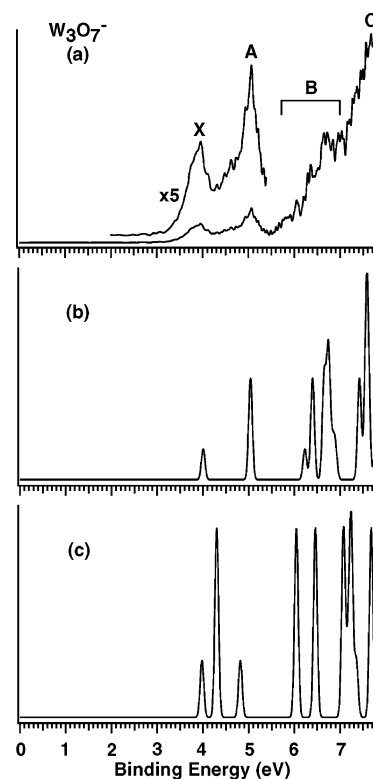


**Figure 9.** (a) LUMO and HOMO pictures of the tribridged  $W_3O_7$  neutral (Figure 4a). (b) The molecular orbitals of the  $W_3O_7^-$  anion (Figure 4e).

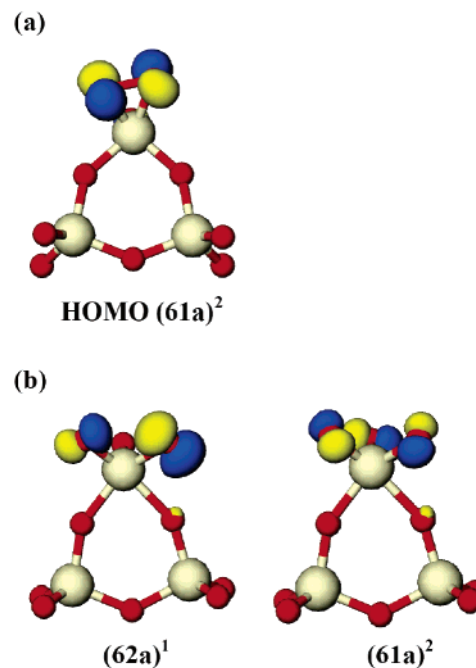
In the  $W_3O_7^-$  anion, the dibridged isomer becomes the global minimum (Figure 4e), with the tribridged isomer being 0.10 eV higher in energy. The dibridged  $W_3O_7^-$  cluster has  $C_s$  ( $^2A'$ ) symmetry with an electron configuration of  $(25a')^2(20a'')^2(26a')^2-(21a'')^2(27a')^2(28a')^2(29a')^1$ . The extra electron in the anion enters the  $29a'$  orbital (Figure 9b), which is a three-center W–W bonding orbital. This is why the dibridged isomer is more stable than the tribridged isomer in the anion because the LUMO of the latter is an antibonding orbital (Figure 9a). The  $28a'$  and  $27a'$  MOs are also primarily W–W bonding orbitals (Figure 9b), and all other MOs below  $27a'$  are O 2p-type orbitals. Detachment from the  $29a'$  orbital results in the X band in the photoelectron spectrum of  $W_3O_7^-$ . The calculated VDE of 4.01 eV (Table 1) is in good agreement with the experimental VDE of the X band (3.90 eV). The next transition is from  $28a'$  ( $\beta$ ) with a calculated VDE of 5.04 eV, which is in excellent agreement with band A (VDE: 5.04 eV). Overall the calculated VDEs from the dibridged  $W_3O_7^-$  isomer agree well with the main PES spectral features, as shown in Figure 10.

However, the tribridged isomer is very close in energy to the dibridged isomer in both the neutral and the anion and would give a similar VDE for the ground-state transition. Thus, we also calculated the VDEs and simulated the spectrum from the tribridged isomer, as compared with the experimental spectrum and that from the dibridged isomer in Figure 10. Even though the first calculated detachment transition of the tribridged isomer is also very close to the X band of the experimental spectrum, the overall PES pattern of the tribridged isomer disagree with the main features of the experimental spectrum. We note that the tribridged isomer may have minor contributions to the observed spectrum. For example, the shoulder on the lower binding energy side of band A may come from the second band of the tribridged isomer. The congested spectral features in the higher binding energy part of the spectrum above 6 eV also indicate that there may be contributions from both isomers. These observations illustrate the sensitivity of the photoelectron spectrum to the cluster structures, lending credence to the dibridged  $W_3O_7^-$  isomer as the global minimum.

**5.1.4.  $W_3O_{10}^-$ .** The ground state of  $W_3O_{10}$  is a closed-shell  $C_1$  ( $^1A$ ) species with an  $O_2$  unit (Figure 5a). The HOMO of this cluster corresponds to the  $\pi^*$  orbital of the O–O moiety,



**Figure 10.** Comparison of the  $W_3O_7^-$  photoelectron spectrum (a) with the simulated spectra from the global minimum dibridged isomer (b) and the tribridged isomer (c).



**Figure 11.** (a) The HOMO picture of neutral  $W_3O_{10}$ . (b) The molecular orbitals of the  $W_3O_{10}^-$  anion.

as shown in Figure 11a. Addition of an electron into the  $\pi^*$  orbital in the anion completely breaks the O–O bond in the ground state of  $W_3O_{10}^-$  (Figure 5c). The isomer with the O–O unit (Figure 5d), in which the extra electron occupies a higher-lying W 5d type orbital, is much higher in energy by 1.57 eV. The ground state of  $W_3O_{10}^-$  has an electron configuration of  $(57a)^2(58a)^2(59a)^2(60a)^2(61a)^2(62a)^1$ . All MOs are of O 2p character; the  $62a$  and  $61a$  MOs are derived from the  $\sigma^*$  and  $\pi^*$  of the  $O_2$  unit, respectively, as shown in Figure 11b.



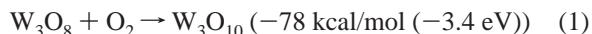
The  $W_3O_{10}^-$  anion has very high electron binding energies, and all detachment transitions occur above 7 eV (Figure 1d). Thus only a very narrow spectral range was observed at 157 nm without any resolved features. The calculated VDE from detachment from the 62a HOMO of  $W_3O_{10}^-$  is 7.09 eV, in excellent agreement with the observed onset of the photoelectron spectrum. Several other detachment channels are within the 157 nm photon energies, as shown in Table 1.

**5.2.  $W_3O_9$ : The Smallest Cluster as Molecular Models for Bulk Tungsten Oxide.**  $W_3O_9$  is a stoichiometric molecule and has been observed to be a major species in the vapor phase of tungsten oxide.<sup>26,27</sup> The large HOMO–LUMO gap observed in our PES spectrum is consistent with the fact that  $W_3O_9$  should be a relatively stable molecule. Each W in  $W_3O_9$  is tetrahedrally coordinated with four O atoms and is chemically saturated, i.e., all W atoms are in the maximum  $W^{6+}$  oxidation state and O atoms are in their maximum  $O^{2-}$  oxidation state. The bridging W–O bonds are single bonds, whereas the terminal O atoms form W=O double bonds. Importantly, we observed that the HOMO–LUMO gap of  $W_3O_9$  is  $\sim 3.4$  eV, which already reaches that of bulk  $WO_3$  (indirect gap,  $\sim 2.6$  eV; direct gap,  $\sim 3.5$ – $3.7$  eV).<sup>45</sup> Previously, we measured that  $WO_3$  molecule has a HOMO–LUMO gap of 1.4 eV,<sup>21</sup> which increases to 2.8 eV in  $W_2O_6$ .<sup>24</sup> It is known that  $WO_3$  has a monoclinic lattice at room temperature. The bulk structure of  $WO_3$  is composed of corner sharing  $WO_6$  octahedra in a  $ReO_3$ -like framework with tilting and distortions of the octahedral, giving structures with lower symmetry than the ideal cubic structure.<sup>46</sup> The calculated bridging W–O bond length in the  $W_3O_9$  is 1.91 Å, which is very close to the bulk value of 1.90 Å. The W–W distance in the  $W_3O_9$  cluster is 3.55 Å, while it is  $\sim 3.7$  Å in the bulk  $WO_3$ . In addition, the calculated W=O vibrational frequencies of the  $W_3O_9$  cluster are quite close to those of terminal W=O from the surface Raman measurements.<sup>47</sup> The unscaled B3LYP Raman band for W=O in  $W_3O_9$  lies at  $\sim 1038$ – $1043$   $cm^{-1}$ , while the surface W=O band is at 950  $cm^{-1}$ . Thus, the  $W_3O_9$  cluster is the smallest species that can be considered as a molecular model for bulk  $WO_3$  from an electronic structure and chemical point of view.

**5.3. Chemical Bonding in Nonstoichiometric  $W_3O_n$  Clusters:  $W_3O_8$  as a Molecular Model for O-Deficient Defect Sites.** The structure of  $W_3O_{10}$  with an  $O_2$  unit is interesting and is consistent with our previous finding on O-rich oxide clusters. We have found that in O-rich oxide clusters  $O_2$  unit can replace an O atom.<sup>21,48,49</sup> Thus,  $W_3O_{10}$  can be viewed as replacing a terminal O atom in the  $D_{3h}$   $W_3O_9$  by an  $O_2$  unit. The O-deficient clusters are more complicated. It appears that there is a competition between W–O single bond and W=O double bond. In the tribridged  $W_3O_8$  global minimum (Figure 3a), there are five terminal W=O units, whereas in the dibridged low-lying isomer (Figure 3b), there are six terminal W=O units. Clearly, two bridging W–O single bonds in the former are favored over the W=O double bond in the latter. In  $W_3O_7$ , a similar competition exists among the low-lying isomers (Figure 4). Again, the tribridged isomer (Figure 4a) with the most bridging W–O bonds is favored.

The global minimum of  $W_3O_8$  (Figure 3a) is formed by removing a terminal O atom from the stoichiometric  $W_3O_9$  cluster, creating a tricoordinated W site. Our MO analysis shows that this W site has a pair of localized d electrons (Figure 8a) and it is essentially a localized  $W^{4+}$  site. Such defect sites are chemically active and may act as catalytic centers in bulk oxides or catalysts.<sup>22</sup> For example, the localized d electrons on the  $W^{4+}$  site may be readily transferred to the  $\pi^*$  orbitals of an

approaching  $O_2$  molecule, making  $W_3O_8$  a molecular model for  $O_2$  activation. In fact, the O-rich  $W_3O_{10}$  cluster can be viewed exactly as the product of  $W_3O_8$  reacting with a  $O_2$  molecule



Our calculation yielded an  $O_2$  chemisorption energy of  $-78$  kcal/mol to the  $W^{4+}$  defect site in  $W_3O_8$ . The O–O distance (1.49 Å) in  $W_3O_{10}$  (Figure 5a) is much longer than that in free  $O_2$  and is close to that in peroxo  $O_2^{2-}$ . We expect that the  $W_3O_8$  cluster can activate other molecules, as well, and may be considered as a molecular model for O-deficient defect sites in tungsten oxides.

## 6. Conclusions

We report a systematic photoelectron spectroscopy and density functional study of a series of tri-tungsten oxide clusters:  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7$ – $10$ ). Detachment features due to W 5d and O 2p features were observed in  $W_3O_7^-$  and  $W_3O_8^-$  with the 5d feature at lower electron binding energies and the O 2p features at very high electron binding energies. A large energy gap was observed in the photoelectron spectrum of  $W_3O_9^-$ , yielding a HOMO–LUMO gap of  $\sim 3.4$  eV for the stoichiometric  $W_3O_9$  molecule. High electron binding energies ( $>7.0$  eV) were observed for  $W_3O_{10}^-$ , suggesting that the  $W_3O_{10}$  neutral cluster is an unusually strong oxidizing agent. Extensive density functional calculations were carried out and combined with the experimental data to elucidate the geometries, electronic structures, and chemical bonding in the  $W_3O_n$  clusters. Our calculations show that  $W_3O_9$  is a  $D_{3h}$  cluster with a  $W_3O_3$  six-membered ring and two terminal W=O units on each W site. The structure of  $W_3O_8$  can be viewed as removing a terminal O atom from  $W_3O_9$ , whereas that of  $W_3O_7$  can be viewed as removing two terminal O atoms from  $W_3O_9$ . The O-rich cluster  $W_3O_{10}$  can be viewed with replacing a terminal O atom in  $W_3O_9$  by an  $O_2$  unit. The  $W_3O_8$  cluster thus contains a tricoordinated W site, which is found to possess a pair of localized 5d electron and is a localized  $W^{4+}$  defect site. It is shown that this defect site can readily react with  $O_2$  to form  $W_3O_{10}$  with a  $-78$  kcal/mol  $O_2$  chemisorption energy. It is suggested that  $W_3O_8$  can be considered as a model for O-deficient defect sites in tungsten oxides.

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