Abstract: Photoelectron spectroscopy (PES) and ab initio calculations are combined to investigate the electronic structure of MO\textsuperscript{n−} clusters (M = Mo, W; n = 3–5). Similar PES spectra were observed between the W and Mo species. A large energy gap between the first and second PES bands was observed for MO\textsuperscript{3−} and correlated with a stable closed-shell MO\textsubscript{3} neutral cluster. The electron binding energies of MO\textsuperscript{n−} increase significantly relative to those of MO\textsuperscript{3−}, and there is also an abrupt spectral pattern change between MO\textsubscript{3−} and MO\textsuperscript{4−}. Both MO\textsuperscript{3−} and MO\textsuperscript{4−} give PES features with extremely high electron binding energies (>5.0 eV) due to oxygen-2p-based orbitals. The experimental results are compared with extensive density functional and ab initio [CCSD(T)] calculations, which were performed to elucidate the electronic and structural evolution for the tungsten oxide clusters. WO\textsubscript{3} is found to be a closed-shell, nonplanar molecule with C\textsubscript{3v} symmetry. WO\textsubscript{3} is shown to have a triplet ground state (\textbf{3}A\textsubscript{2}) with D\textsubscript{2d} symmetry, whereas WO\textsubscript{5} is found to be an unusual charge-transfer complex, \((\text{O}_2\textsuperscript{−})\text{WO}_3\textsuperscript{−}\). WO\textsubscript{4} and WO\textsubscript{5} are shown to possess W\textsuperscript{5+} and O\textsuperscript{2−} radical characters, respectively.

Introduction

Transition-metal oxides are widely used in important industrial processes, both as catalysts and as catalytic supports. In particular, the catalytic activity of tungsten oxides\textsuperscript{1–6} and molybdenum oxides\textsuperscript{7–9} have been extensively studied. The identification of active sites in transition-metal oxide catalysts is difficult and, due to their extreme complexity, often leads to differing hypotheses as to the molecular mode of action. As a first step in developing a comprehensive understanding of complex catalytic processes on transition-metal oxides, we are studying the structure and reactivity of isolated transition-metal oxide clusters. Gas-phase studies, coupled with reliable theoretical calculations, can provide powerful insight into the nature of active species in catalysis at the molecular level.\textsuperscript{10,11}

We are interested in probing the electronic structure of transition-metal oxide clusters aiming at providing molecular models and mechanistic insight for the oxide catalysts as well as providing experimental data for the benchmark of theoretical methods.\textsuperscript{12–18} Among our previous works is a study on a series of CrO\textsubscript{3} and CrO\textsubscript{n−} clusters.\textsuperscript{19} In the present work, we investigate the electronic structure and chemical bonding of the heavier group VI MO\textsubscript{3} and MO\textsubscript{n−} species (M = W, Mo; n = 3–5), using anion photoelectron spectroscopy (PES) and ab initio and density functional theory (DFT) calculations.

For the mono-tungsten oxide clusters, high-resolution spectroscopic data are available for WO\textsubscript{3},\textsuperscript{19–25} WO\textsubscript{4},\textsuperscript{26} and WO\textsubscript{5}.\textsuperscript{27–29}
A vibrationally resolved photoelectron spectrum has been reported for WO$_4$.

The electron affinity of the molecule WO$_3$ has been measured using different methods with a wide spread of values (3.33–3.94 eV).

Recently, Stolicic, Kim, and Gantefor (SKG) reported photoelectron spectra of WO$_5^-$ and WO$_4^-$ showing a dramatic decrease of electron binding energies from WO$_3^-$ to WO$_3^-$ and suggested a transition from "atomic-to-molecular adsorption of oxygen" from WO$_3^-$ to WO$_4^-$.

This observation was surprising and in contrast to that from our previously reported CrO$_5^-$ series, where a dramatic increase in electron binding energies was observed from CrO$_5^-$ to CrO$_4^-$.

Previous gas-phase studies on mono-molybdenum oxide clusters include photoelectron spectroscopy of MoO$^-$ and reactions of MoO$_4^-$ with CO and CO$_2$ as well as infrared spectroscopy of MoO$_2$, MoO$_2^-$, and MoO$_3$ in a neon matrix.

The current study represents a continuation of our research interest in oxide clusters.

Experimental Section

Experimental Method.

The experiments were carried out using a magnetic-bottle-type PES apparatus equipped with a laser vaporization supersonic cluster source, details of which have been described previously.

Briefly, the MO$_x$ cluster anions (M = W, Mo) were produced by laser vaporization of a pure metal target in the presence of a helium carrier gas seeded with 0.5% O. Various MO$_n^-$ clusters were produced from the source and analyzed using a time-of-flight mass spectrometer. The MO$_n^-$ (n = 3–5) species of interest were each mass-selected and decelerated before being photodetached. Two detachment photon energies were used in the current study: 266 (4.661 eV) and 193 nm (6.424 eV). Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The photoelectron spectra were calibrated using the known photon energies were used in the current study: 266 (4.661 eV) and 213 (4.036 eV). Vertical detachment energies (VDEs) for WO$_3$ were calculated using the TD-DFT method.

Harmonic frequency calculations were done to verify that the stationary points are minima. Vertical detachment energies (VDEs) for WO$_4$ were calculated using the generalized Koopman's theorem by adding a correction term to the eigenvalues of the anions. The correction term was estimated by eq

\[ \delta E = E_1 - E_2 - E_{\text{HOMO}} \]

where \( \delta E \) is the correction term, \( E_1 \) and \( E_2 \) are the total energies of the anion and neutral in their ground states at the anion equilibrium geometry, and finally \( E_{\text{HOMO}} \) corresponds to the eigenvalue of the highest


occupied molecular orbital of the anion. All of the DFT calculations were carried out with Gaussian 03.46

We also did a set of calculations using the CCSD(T) method.47 Geometries were optimized with the “aug-cc-pVDZ” for WO3, WO4, WO5, and WO3−. For WO3 and WO3−, we used the B3LYP geometries as described above. We also did calculations on WO4 and WO4− with the B3LYP geometries. The CCSD(T) calculations were done starting from restricted Hartree–Fock wave functions for both the open- and closed-shell molecules. The closed-shell calculations were done with the RCCSD(T) approach, and the open-shell calculations were done with the UCCSD(T) approach. All of the coupled-cluster calculations were carried out using MOLPRO package.48

Experimental Results

WO3−. Photoelectron spectra of WO3− are shown in Figure 1. Only one band (X) was observed at 266 nm (Figure 1a) with discernible fine features. A VDE of 3.83 eV was obtained from the peak maximum. Since no well-resolved vibrational structures were obtained, the adiabatic detachment energy (ADE) was evaluated from the well-defined onset of band X by drawing a straight line at the leading edge of the band and then adding the instrumental resolution to the intersection with the binding energy axis. The ADE thus obtained was 3.62 ± 0.05 eV, which represents the electron affinity of neutral WO3. The 193 nm spectrum (Figure 1b) revealed four additional bands at higher binding energies: A (5.22 eV), B (5.48 eV), C (5.68 eV), and D (5.98 eV). The observed ADE and VDEs for WO3− are collected in Table 1. The current 193 nm spectrum agrees with that by SKG; the higher binding energy features in the current data were slightly better resolved. SKG also presented a vibrationally resolved spectrum for the X band with a 30 meV spacing,32 but they did not report ADE and VDE values for any spectral features.

WO4−. In contrast to WO3−, WO4− possesses extremely high electron binding energies and only 193 nm photons could be used for photodetachment, as shown in Figures 2a. A complex spectrum was observed with three identifiable bands (X, A, and B). The lowest energy band (X) was broad with a reasonably sharp onset, which yielded an ADE of 5.30 eV. The band maximum gave a VDE of 5.44 eV for the ground-state transition. Band A with a VDE of 5.88 eV was intense and relatively sharp, but there seemed to be shoulders on both sides of band A. Band B at 6.24 eV was relatively weak. The observed ADE and VDEs for WO4− are also given in Table 1.

We specifically note that the current spectrum of WO4− is completely different from that reported previously by SKG.32 SKG only presented a spectrum at 266 nm for WO4− that showed a single band with relatively poor signal-to-noise ratios in the binding energy range between 2 and 3 eV. We were unable to reproduce the SKG spectrum, despite extensive experimental efforts using different detachment photon energies and different source conditions. Our data suggested that a single 266 nm photon would not be sufficient to detach WO4−.

WO5−. WO5− also possesses very high electron binding energies. Its PES spectrum at 193 nm (Figure 2b) exhibited a broad, partially resolved band between ~5.1 and 6 eV with a very sharp peak (C) at 6.16 eV. Three overlapping features may be tentatively identified within the broad band, X, A, and B, among which the B band at 5.74 eV was well defined. Band X appeared as a shoulder in the lower binding energy side, and

| WO3− | 3.62 (5) | 3.83 (3) | 5.22 (3) | 5.48 (2) | 5.68 (2) | 5.98 (2) |
| WO4− | 5.30 (5) | 5.44 (3) | 5.88 (2) | 6.24 (2) |
| WO5− | 5.1 (1) | ~5.3 | 5.50 (3) | 5.74 (2) | 6.16 (2) |
| MoO3− | 3.135 (15) | 3.33 (5) | 5.13 (5) | 5.35 (3) | 5.63 (2) |
| MoO4− | 5.20 (7) | 5.45 (5) | 5.82 (2) | 6.02 (3) |
| MoO5− | 5.10 (7) | 5.40 (5) | 5.70 (5) | 5.93 (2) | 6.20 (5) |

*All energies are in eV. Numbers in parentheses represent the experimental uncertainties in the last digits.
an ADE of ~5.1 eV was estimated from the threshold. The ADE and VDEs for WO₅⁻ are also given in Table 1.

MoO₃⁻ (n = 3–5). Photoelectron spectra of MoO₃⁻ (n = 3–5) at 193 nm are shown in Figure 3. Very similar spectra were observed for the MoO₃⁻ species compared to those of WO₄⁻. A vibrationally resolved spectrum with a spacing of 230 cm⁻¹ was obtained for the ground-state transition of MoO₃⁻ at 355 nm, as shown in the inset in Figure 3a. This vibrational spacing is similar to that observed by SKG for the ground-state band of WO₄⁻.32 In the 193 nm spectrum of MoO₃⁻, a large energy gap was observed with three more bands appearing at higher binding energies (A, B, C). For MoO₄⁻ and MoO₅⁻ there is a one-to-one correspondence between the spectral features of the Mo and W clusters. All the observed ADEs and VDEs for MoO₃⁻ (n = 3–5) are given in Table 1, along with those for WO₃⁻.

Computational Results

Optimized ground-state geometries of WO₃⁻, WO₄⁻, and WO₅⁻ and their anions are presented in Figure 4, and those of a low-lying isomer of WO₄⁻ and WO₅⁻ are also given. Theoretical ADEs and VDEs at the DFT and CCSD(T) levels are given in Table 2.

Table 2. B3-LYP and CCSD(T) Calculated Detachment Energies (eV) for WO₃⁻, WO₄⁻, and WO₅⁻

<table>
<thead>
<tr>
<th>Detachment channel</th>
<th>B3-LYP</th>
<th>CCSD(T)</th>
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<tr>
<td></td>
<td>ADE</td>
<td>VDE (a) (singlet)</td>
</tr>
<tr>
<td>WO₃⁻&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7a¹)⁻&lt;sup&gt;1&lt;/sup&gt;</td>
<td>3.45</td>
<td>3.83</td>
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<tr>
<td>(1a₂)⁻&lt;sup&gt;1&lt;/sup&gt;</td>
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<td>5.35</td>
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<tr>
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<td>5.44</td>
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<td>7.69</td>
<td>6.53</td>
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<tr>
<td>WO₄⁻&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
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<tr>
<td>(17a⁻)⁻&lt;sup&gt;1&lt;/sup&gt;</td>
<td>6.47</td>
<td>6.44</td>
</tr>
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<sup>a</sup> At aug-cc-pVTZ-CCSD(T) level. <sup>b</sup> Numbers in the parentheses at aug-cc-pVDZ-CCSD(T) level. <sup>c</sup> The valent electronic configuration of WO₃⁻ is 6a₁⁻e¹e¹a₂⁺(7a₁⁻)⁺. <sup>d</sup> The valent electronic configuration of WO₄⁻ is 9a₁⁻4b₁⁻4b₂⁻1a₂⁻5b₁⁻5b₂⁻6b₂⁻10a⁻2a₂⁻6b₁⁻. <sup>e</sup> ADE and VDE of WO₅⁻ at the DFT geometry are 5.34 (5.17) and 5.51 eV, respectively. <sup>f</sup> The valent electronic configuration of WO₅⁻ is 16a₁⁻6a₂⁻7a₂⁻17a⁻18a⁻8a⁻19a⁻20a⁻.<sup>c</sup> and 11.8° at the aug-cc-pVTZ-CCSD(T) level. The planar D₃h structure is a transition state for inversion with a low out-of-plane imaginary vibrational mode (108.4 cm⁻¹) and a small barrier height (1.2 kcal/mol). The neutral WO₃ molecule (2) is
closed shell ($^1A_1$) and also has $C_{3v}$ symmetry. The lowest triplet state of WO$_3$ ($^3A_2$) is 1.71 eV higher in energy at the B3LYP level. The W–O bond length for neutral WO$_3$ (1.725 Å) [1.737 Å at the aug-cc-pVTZ/CCSD(T) level and 1.763 Å at the aug-cc-pVQZ/CCSD(T) level] is decreased by 0.03–0.04 Å as compared to the anion. Significant changes occur in the bond angles of neutral WO$_3$: the $\zeta$WO bond angle decreases to 107.7° at the B3LYP level (108.3° at CCSD(T)/aug-cc-pVTZ), which is near the tetrahedral bond angle, and the out-of-plane angle increases to 21.1° (20.6°, CCSD(T)/aug-cc-pVTZ), showing an increased pyramidalization at the central W site. Consistent with this change in geometry, the umbrella inversion of the neutral WO$_3$ at the B3LYP level has a much larger barrier (16.1 kcal/mol) than that of the corresponding anion. The W–O bond length in WO$_3$ at 1.72 Å is similar to a wide range of oxo bond lengths for oxo–tungsten compounds that we have calculated, consistent with a simple description of the bonding in this molecule as three W=O double bonds.

**WO$_4$** and **WO$_5$.** A range of isomers was studied in the search of the ground states for WO$_4$ and its anion. The two lowest energy isomers are given in Figure 4 (3–6). All methods agree that the ground state of WO$_4^-$ was $^3B_2$ with $C_2v$ symmetry, with the four oxygen atoms bonded to tungsten in a distorted tetrahedron (3). The distortion to $C_{2v}$ symmetry from $T_d$ symmetry leads to two kinds of oxygen atoms, two with longer bonds (1.836 Å) at the B3LYP level [1.868 Å at CCSD(T)/aug-cc-pVTZ], which we label as oxyl (–O$^-$)–O$_2$–O$_2$–O$^-$, and two as oxo (O=O) oxygens with shorter bonds [1.757 Å at the B3LYP level; 1.789 Å at CCSD(T)/aug-cc-pVQZ]. The B3LYP $\zeta$WO bond angle between the oxyl oxygens shows significant deviation from the tetrahedral value, 100.3° at the B3LYP level [99.7° at CCSD(T)/aug-cc-pVTZ], whereas the $\zeta$WO bond angle between the oxo oxygens is near tetrahedral, 110.9° at the B3LYP level [111.3° at CCSD(T)/aug-cc-pVQZ]. The ground state of WO$_4^-$ is well separated in energy (by 2.04 eV) from the second stable isomer with a di-oxo (O=O) bond (5).

The calculation of the ground state of neutral WO$_4$ (4) was particularly difficult due to symmetry-breaking issues, which in part manifest themselves in very small HOMO–LUMO gaps. There are a number of possible geometries to consider for WO$_4$. In analogy to the anion, WO$_4$ can be described as either a distorted tetrahedral molecule or $O_2$ complexed to a bent WO$_2$. It is predicted to be a triplet derived from $T_d$ symmetry and must distort due to the Jahn–Teller effect. The geometry at the B3LYP level converged to a symmetry-broken triplet ($^3A_1$) minima with $C_1$ symmetry. Whereas the triplet $D_{2d}$ and $C_{2v}$ structures for WO$_4$ were second-order stationary points, the triplet $C_1$ structure was a first-order one leading to the $C_1$ minimum. The energy difference between all these structures was less than 0.03 eV. As mentioned earlier, B3LYP failed to yield the delocalized ($D_{2d}$) structure, which is a resonance hybrid of the two localized $C_{2v}$ structures. This failure can be traced back to the mixing of HF-exchange in the functional. Calculations by PW91xPW91c resulted in a $D_{2d}$ ($^3A_2$) ground state for neutral WO$_4$ with delocalized W–O bonds (1.802 Å); no other minima were identified. In addition, other functionals without any HF exchange also yielded a $D_{2d}$ minimum structure. Again, convergence of the wave function was hampered by the near degeneracy of the HOMO and LUMO orbitals. We also performed detailed calculations on WO$_4$ starting from the B3LYP geometries at the CCSD(T)/aug-cc-pVQZ level. The lowest energy structure is the $D_{2d}$ triplet with a W–O distance of 1.828 Å and a $\zeta$WO bond angle of 102.2°, significantly distorted from the ideal $T_d$ geometry. Of real interest is that the W–O bond distance is not that of an oxo O but is more like that of an oxyl (–O$^-$). The other structures with lower symmetry were all higher in energy at the CCSD(T) level. Thus, we conclude that the ground state of WO$_4$ is $^3A_2$ with $D_{2d}$ symmetry with the spin density shared on all four oxygen atoms.

Other possible isomers beyond those derived from $T_d$ WO$_4$ are higher in energy. The neutral di-oxo oxygen isomer (6) is 0.39 eV higher in energy than the ground state at the B3LYP level (Figure 4). Our optimized structures differ from the speculation by SKG, who suggested that WO$_4^-$ may have a peroxyl-type structure with only one oxygen in the O$_2$ moiety connected to W. We found no stationary point for a peroxyl structure, as all such initial structures at all DFT levels of theory collapsed to either the distorted $T_d$ ground state or to the di-oxo isomer on optimization.

**WO$_5^-$ and **WO$_5$.** An extensive search of the potential-energy surface of WO$_5^-$ and WO$_5$ at the B3LYP level yielded only one di-oxo type of stable structural arrangement (7 and 8). The ground state of WO$_5^-$ ($^3A'$) and WO$_5$ ($^3A''$) can be viewed as O$_2^-$ interacting with a WO$_3$ fragment and O$_2^-$ interacting with a WO$_3^-$ fragment, respectively. The O$_2^-$ is oriented parallel to one of the W–O bond vectors in both the neutral and the anion. Support for this description comes from the structural parameters. The O–O bond lengths in 7 and in 8 are 1.342 and 1.312 Å, respectively, very close to the O–O bond length in molecular O$_2^-$ (1.352 Å) at the B3LYP level. The W–O bond lengths in the WO$_3$ fragment in WO$_5^-$ are 1.750 and 1.751 Å, only slightly longer (0.025 Å) than the W–O bond length in WO$_3$ (1.725 Å). Correspondingly, the bond distances of the O$_2$ moiety to W in 7 are 2.090 and 2.288 Å, much longer than the W–O single bonds, which are in the range of 1.9 Å based on a large number of structures that we have calculated. No significant structural change in the O–O moiety was predicted on removal of an electron to form neutral WO$_5$ except for the slippage of the O$_2$ unit toward one of the o xo atoms (8). However, in the WO$_3$ moiety, one of the W–O bonds is significantly elongated (1.884 Å). This long bond is much longer than an oxo W=O bond and is very similar to that of a W–O single bond. This suggests a major electronic and structural reorganization upon electron detachment.

**Discussion.**

Our discussion will mainly focus on the WO$_3$/WO$_3^-$ series for which extensive theoretical calculations were carried out. The structures and bonding in MoO$_3$/MoO$_3^-$ are expected to be similar to the W counterparts, as can be seen from their similar PES spectra.

**Stoichiometric Molecule: WO$_3$.** W has a 5d$^4$6s$^2$ valence electron configuration and forms a stoichiometric molecule with the three O atoms in WO$_3$, which is a stable gaseous species. However, the molecular properties of the WO$_3$ molecule are not well understood, and there is no definitive spectroscopic data about WO$_3$ in the gas phase. For example, the electron affinity of WO$_3$ was widely scattered in the literature. The most recent review on atomic and molecular electron affinities...
lists a value of 3.33$^{+0.08}_{-0.15}$ eV for WO$_3$ from a threshold photodetachment experiment. In the work by SKG, the electron affinity of WO$_3$ was not reported. Our photoelectron spectra yielded an ADE of 3.62 ± 0.05 eV for WO$_3$ determined from the detachment threshold of the 266 nm spectrum of WO$_3^-$. Provided that there is a measurable Franck-Condon factor for 0–0 detachment transition, our measurement should represent an accurate electron affinity for WO$_3$.

The ground state of WO$_3$ was predicted to be closed shell ($^1A_1$, $C_s$) with a valence electron configuration of 6a$^2$6e$^2$1a$_2^2$, which are all primarily O 2p-type orbitals. The WO$_3^-$ anion was predicted to be a doublet ($^2A_1$, $C_s$) with the extra electron occupying the 7a$_1$ LUMO of WO$_3$, giving rise to an electron configuration of 6a$^2$6e$^2$1a$_2^2$7a$_1^1$ for WO$_3^-$. The 7a$_1$ MO is primarily a nonbonding d$_z^2$ orbital localized on W. Occupation of this MO induces a significant planarization in WO$_3^-$ in which W is only slightly out of the plane defined by the three oxygen atoms whereas in the neutral molecule W is substantially more out-of-plane (Figure 4). There were no significant changes in the W—O bond length between WO$_3$ and WO$_3^-$. Therefore, on photodetachment from the anion, the inversion mode of the neutral is expected to be active. The ground-state detachment transition (X) of WO$_3^-$ was indeed very broad, consistent with an unresolved vibrational progression of a low-frequency inversion mode. The calculated inversion mode frequency for WO$_3$ at the B3LYP level is 278 cm$^{-1}$, consistent with the vibrational spacing observed in the previous PES study of WO$_3^-$ by SKG (30 meV or $\sim$240 cm$^{-1}$). In the current study we observed a broad vibrational progression with a spacing of 230 ± 30 cm$^{-1}$ for the ground-state transition of MoO$_3^-$. (Figure 3a). Similar to WO$_3^-$, this should be due to the inversion mode of $C_s$ of MoO$_3$, which we calculated to be 284 cm$^{-1}$ at the LDA level.

The second PES band in WO$_3^-$ (A in Figure 1b) should correspond to the first triplet excited state of WO$_3$ due to removal of an electron from the 1a$_2$ MO, i.e., the HOMO of neutral WO$_3$. The A–X energy difference represents an approximate experimental measure of the HOMO–LUMO gap for the neutral molecule. We measured a HOMO–LUMO gap of 1.4 eV for WO$_3$ and 1.8 eV for MoO$_3$. The calculated ADE for the ground-state transition of WO$_3^-$ was 3.83 eV at the B3LYP level (Table 2), in excellent agreement with the experimental result. The CCSD(T)/aug-cc-pVTZ value for the VDE is 3.67 eV. The theoretical ADE for the ground-state transition at both B3LYP and CCSD(T) (Table 2) is also in reasonable agreement with the experimental measurement. Detachment from the fully occupied MOs will each lead to a triplet and singlet final state. The calculated VDEs for several valence MOs within our photon energy range are given in Table 2. Clearly, there are more detachment transitions in the higher binding energy side in the 193 nm spectrum of WO$_3^-$ (Figure 1b) than were resolved. Overall, the calculated spectral pattern is in good agreement with the experimental PES spectra.

**Diradical WO$_4$ and Delocalized Electrons.** WO$_4^-$, as well as MoO$_4^-$, possesses extremely high binding energies, which can be accessed only at 193 nm. Thus, WO$_4$ and MoO$_4$ belong to the category of strong oxidizers called superhalogens. We found that many O-rich transition-metal clusters possess such high electron binding energies, which is a consequence of delocalization of the extra electron over several O centers. The structure of the WO$_4^-$ anion can be understood from the closed-shell tetrahedral WO$_4^-$ units, which exist in solids, such as Na$_2$WO$_4$. Removal of an electron from the $T_d$ WO$_4^-$ results in a Jahn–Teller unstable WO$_4^-$, which distorts to a lower symmetry $C_2v$ structure. All of the DFT functionals that we used gave similar results for the structure of WO$_4^-$ as did the CCSD(T) method. The $C_2v$ global minimum of WO$_4^-$ was found to be well separated in energy from the second lowest energy isomer, which consists of a di-oxygen fragment and two $\omega$=O oxo units ($\delta$ in Figure 4).

The ground state of WO$_4^-$ anion is $^2B_2$ with a valence electronic configuration of 1a$_2^2$5b$_2^2$5b$_1^2$10a$_1^2$2a$_2^2$6b$_2^2$. In the spin-unrestricted formalism. All these MOs are of O 2p type. Note that the unpaired spin is not in the HOMO. The negative charge in WO$_4^-$ is delocalized over the two oxyl O atoms, significantly stabilizing the corresponding MO.

At the B3LYP level, the converged wave function showed that the first electron detachment is from the 6b$_1^0$ orbital, giving a VDE of 5.66 eV, in reasonable agreement with the experimental value of 5.44 ± 0.03 eV. After orbital and geometry relaxation, we obtained a triplet ground state $^3A_1$ ($D_{2d}$) with delocalized W–O bonding for neutral WO$_4$, which is quite unusual and can be considered as a diradical. As shown in Table 2, the computed VDE values for transitions to other triplet neutral states are 5.91, 5.94, and 6.21 eV, whereas those for the singlet states are 5.69, 6.26, 6.32, and 6.63 eV. All of these transitions agreed well with the PES spectrum of WO$_4^-$ (Figure 2a). Although only three bands are labeled, there are clearly more unresolved bands in the spectrum between the three main bands. At the CCSD(T)/aug-cc-pVTZ level, the VDE for the ground-state transition was calculated to be 5.25 eV using the calculated geometry at the CCSD(T)/aug-cc-pVQZ level. The calculated VDE using the DFT geometry for WO$_4^-$ is 5.51 eV. These results show that the calculated electron binding energies for this species are very sensitive to the geometry. The calculated ADE values are 5.22 eV at the B3LYP level and 5.11 eV at the CCSD(T)/aug-cc-pVTZ level (including PW91PW91 ZPE = 0.29 kcal/mol).

Our PES spectrum of WO$_4^-$ differs completely from that reported recently by SKG. The spectrum by SKG was taken at 266 nm, showing a single weak and broad band between 2 and 3 eV. The band appeared to have fine structures with a 180 meV spacing, but the signal-to-noise ratio of the spectrum was relatively low. The authors interpreted the 180 meV spacing as O–O vibration and concluded that there was “a transition from atomic-to-molecular adsorption of oxygen on tungsten atom” from WO$_3$ to WO$_4$. We made extensive efforts to reproduce the SKG spectrum, but we were not able to observe any photoemission signals at the low binding energy range (Figure 2a). We note that the (O$_2$)WO$_2^-$ species has been assigned from a matrix infrared spectroscopy study under cryogenic condition at 4 K. Our calculations showed that such a species was much higher in energy (by 2.04 eV) than the global minimum structure (Figure 4). Thus, the (O$_2$)WO$_2^-$ isomer was unlikely to be populated in the cluster beam with high electron binding energies, which is a consequence of delocalization of the extra electron over several O centers.


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- an isomer was predicted to be 3.43 eV, which is much higher than that reported by SKG (~2.5 eV). Our spectrum showed no photoemission signals around 3.43 eV (Figure 2a), suggesting that the (O2)WO2 isomer was not populated in our experiment at any observable abundance, consistent with the fact that it is 2.04 eV higher in energy than the lowest global minimum WO3. Our experimental and theoretical results suggested that the spectrum reported by SKG could not be due to the higher energy (O2)WO2 isomer of WO3.

WO3: Charge-Transfer Complex. The WO3 anion has C2 symmetry with an O–O moiety bonded to WO3. It has a 3A’ ground electronic state with a valence electron configuration of 16a6a7a117a218a28a219a39a52 in the spin-unrestricted formalism. Note that the excess spin does not arise from the HOMO. In fact, it is five orbitals below the HOMO (9a′), which is an oxygen lone pair. The structural parameters of WO3 (7, Figure 4) are consistent with an O2− unit interacting with a WO3 fragment, (O2−)WO3. This was borne out by the calculated spin density (Figure 5), which shows that the excess spin is almost completely localized on the O2− fragment. The orbital and geometry description of WO3− is clearly that of O2− bonded to WO3.

The first calculated VDE (5.35 eV) at the B3LYP level arises from the 9a′ orbital, in excellent agreement with the experimental VDE value of band X (5.3 eV, Figure 2b). This detachment channel removes an electron from the WO3 fragment to form a distorted WO3+ and does not substantially perturb the O2− unit. As a result, in the neutral WO3 except for the lateral shift of the O2− unit and a slight shortening of the O–O distance there were no major changes in the di-oxygen interaction with W. Consequently, neutral WO3 can be described as O2− interacting with WO3+, essentially a charge-transfer complex, (O2−)(WO3+). The spin density in WO3 is consistent with the charge-transfer description, as shown in Figure 5c. One of the W–O bonds in the WO3+ fragment is considerably elongated in WO3. This large geometrical change is consistent with the relatively broad ground-state detachment band observed for WO3− (X in Figure 2b). The calculated ADE at the B3LYP level for WO3− is 4.93 eV (Table 2), as compared to the experimental value of 5.1 ± 0.1 eV. The CCSD(T)/aug-cc-pVTZ ADE of 5.12 eV (including a ΔZPE(PW91PW91) of 0.40 kcal/mol) is in excellent agreement with the experimental value. The calculated VDEs from all the valence MOs within our photon energy are listed in Table 2. The overall theoretical VDE pattern agrees well with the PES spectrum.

Chemical Bonding in WO3 and WO3− (n = 3–5). The chemical bonding in the mono-tungsten oxide species can be understood conveniently using the valence-bond description as shown in Scheme 1. In WO3 (C3v) the six valence electrons of W form three W=O double bonds and a stable closed-shell molecule with a large HOMO–LUMO gap. In the anion the additional electron occupies the nonbonding d2 orbital of W.

In neutral WO3 the two unpaired electrons are completely delocalized over all four oxygen atoms. The D2d ground state of WO3 can be described as a resonance hybrid of two equivalent C2v structures. Addition of an electron to WO3 stabilizes the C2v structure, leading to two W=O double bonds and delocalization of the extra charge over two O atoms. Whereas the short bonds can be described as being o xo bonds with 2c–2e dz2−pz bonding, the long bonds can be described as two single W–O bonds resonantly stabilized by the additional electron in a π system just as that found in CO2−. We calculated the energy for addition of O2 to WO3 to form WO3+ to be exothermic by 82.8 kcal/mol (3.59 eV) at the CCSD(T)/aug-cc-pVTZ level, indicating the formation of very strong W–O bonds. Taking the O2 bond energy of 120 kcal/mol and assuming no change in the two original W–O bond energies and complete breaking of the O=O bond suggest that the average bond energy of the new W–O bond energies is 102 kcal/mol. Addition of O2− to WO3 can be estimated from our values and the electron affinity of O2 (0.45 eV) to be highly exothermic by 194.7 kcal/mol or 8.44 eV [−3.59 + (−5.30) + 0.45]!

The chemical bonding in WO3− and WO3 is very interesting and unexpected. The structure of WO3− shows that it is a complex formed by WO3 and O2− fragments. The three short W=O bonds (1.751 Å) are only slightly elongated as compared to those in WO3 (1.725 Å) (Figure 4), whereas the distances between O2− and W (2.090 and 2.288 Å) are much longer than those expected for W=O single bonds (1.90 Å). The O=O bond (1.342 Å) in WO3− was similar to that in free O2− (1.352 Å). In WO3, one unpaired electron is localized on the O2− fragment as in the case of the anion, and the other unpaired electron is localized on one of the O atoms of WO3, giving rise to the unusual charge-transfer complex, (O2−)WO3+. We calculated the energy for addition of O2 to WO3 to form WO3+ to be exothermic by only 13.7 kcal/mol (0.59 eV) at the CCSD(T)/aug-cc-pVTZ level. This exothermicity is 3 eV less than that of WO3 plus O2 and shows that only a weak complex of O2 with WO3 is formed because the three o xo bonds in WO3 have consumed all the available valency of W. In fact, the only way for O2 to bind to WO3 is for charge exchange to occur, leading to formation of a WO3+O2− triplet charge-transfer complex. Addition of O2− to WO3 occurs with a much higher exothermicity of 121.8 kcal/mol or 5.28 eV [−0.59 + (−5.14) + 0.45].
Comparison between WO₄ and MoO₄. Both WO₄ and WO₃ and their anions are “oxygen-excessive” species. Superxo-type ground-state structures might have been expected for such species, where the presence of an O=O bond could provide further stabilization. However, as clearly shown from our combined experimental and theoretical study, tungsten preferred tetrahedral coordination with oxygen in both WO₄ and WO₄⁻, and no O−O bond was observed. In WO₂ two oxygen radical units, one O⁺ (from W=O) and one O₂⁻, exist. For the WO₅⁻ anion the O₂⁻ radical character is retained. Both WO₃ and WO₅⁻ may still be viewed as tetracoordinated if the O₂⁻ group is considered as a single species. The observations of oxygen radical character (W=O⁺ and O₂⁻) and tetracoordinate tungsten in mono-tungsten oxide clusters are highly interesting and unexpected. Tetrahedral WO₄⁻² species are stable structural units in bulk crystalline materials such as Na₂WO₄, CaWO₄, and Al₂(WO₄)₃. Note that a W=W bond (160.6 kcal/mol, 6.96 eV) is much stronger than an O=O bond (119.1 kcal/mol, 5.17 eV), which makes W=W bond formation energetically more favorable than O=O bond formation in WO₈ and WO₈⁻. For comparison, the MoO bond is 133.9 kcal/mol and the CrO bond is 102.6 kcal/mol. The differences in bond energy may explain why the ground-state structure of CrO₄ is different from that of WO₄. CrO₄ possesses an O₂⁻ unit, whereas WO₄ preferred tetrahedral coordination with delocalized electrons. This is consistent with the fact that the Cr=O bond energy is less than that of O₂ whereas the opposite is true for W=W and O₂. As the bond energy for Mo=O is greater than that for O₂, we would expect MoO₂ to behave like WO₂ rather than CrO₂. The photoelectron spectra for MoO₃⁻ (n = 3−5) species show striking similarities to those of WO₃⁻, but they were much different from those of CrO₄⁻.¹⁷

Conclusions

A combined photoelectron spectroscopic and theoretical study was carried out on mono-tungsten and molybdenum oxide clusters MOₙ⁻ (M = W, Mo; n = 3−5). Well-resolved PES spectral features were obtained and compared with theoretical calculations. A large energy gap was observed for the MO₅⁻ species between its low binding energy metal-d-based band and high binding energy oxygen-2p-based bands, characteristic of a stable closed-shell MO₉ neutral cluster. A dramatic increase in electron binding energies was observed between MO₃⁻ and MO₇⁻: the ADEs measured for WO₅⁻ and MoO₅⁻ are 3.26 and 3.135 eV, respectively, and they increased to 5.30 and 5.20 eV for WO₆⁻ and MoO₆⁻. The ADEs of the MO₅⁻ species are also extremely high, similar to those of the MO₇⁻ species. Only oxygen-2p-based detachment features were observed for MO₇⁻ and MO₉⁻. Extensive electronic structure calculations at the density functional theory and CCSD(T) levels with large basis sets were performed on WO₅⁻ and WO₈⁻ (n = 3−5) to elucidate the electronic and structural evolution. WO₅⁻ and WO₇ were found to have C₃v structures with three oxo W=O bonds. A tetrahedral coordination environment about tungsten was found for WO₄ and WO₆⁻: WO₄⁻ has C₃ᵥ symmetry with two W=O oxo units and the extra charge delocalized on the other two W=O units, whereas WO₆ has D₅h symmetry and two unpaired electrons each delocalized over two W=O units. WO₅⁻ can be viewed as an O₂⁻ interacting with a WO₃ unit, whereas neutral WO₃ is found to be a unprecedented charge-transfer complex, (O₂⁻)WO₅⁻. The observation of radical characters (W=O⁺ and O₂⁻) in WO₄ and WO₅ may be relevant to the catalytic activity and selectivity of tungsten oxide catalysts.

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