

Calculation of Photoelectron Spectra of Molybdenum and Tungsten Complexes Using Green's Functions Methods

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Green's functions calculations are presented for several complexes of molybdenum and tungsten, two metals that are similar structurally but display subtle, but significant, differences in electronic structure. Outer valence Green's functions IPs for $M(\text{CO})_6$, $M(\text{Me})_6$, $M\text{H}_6$, $[\text{MCl}_4\text{O}]^-$, and $[\text{MO}_4]^-$ ($M = \text{Mo}, \text{W}$) are generally within ± 0.2 eV of available experimental photoelectron spectra. The calculations show that electrons in M–L bonding orbitals are ejected at lower energies for Mo while the detachment energy for electrons in d orbitals varies with metal and complex. For the metal carbonyls, the quasiparticle picture assumed in OVGf breaks down for the inner valence π CO molecular orbitals due to the coupling of two-hole–one-particle charge transfer states to the one-hole states. Incorporation of the 2h1p states through a Tamm–Dancoff approximation calculation accurately represents the band due to detachment from these molecular orbitals. Though the ordering of IPs for Green's functions methods and DFT Koopmans' theorem IPs is similar for the highest IPs for most compounds considered, the breakdown of the quasiparticle picture for the metal carbonyls suggests that scaling of the latter values may result in a fortuitous or incorrect assignment of experimental VDEs.

Introduction

An understanding of the electronic structure of transition metal complexes is important for discerning the roles metals play in biological systems, catalysis, and oxidation/reduction. Photoelectron spectroscopy (PES) is a valuable tool in the experimental elucidation of the electronic structure of chemical systems.^{1,2} Direct observation of valence ionization potentials (IPs) allows for the construction of a diagram of the orbital energies that can be interpreted with the help of theory. As a first approximation, vertical IPs can be estimated theoretically using the molecular orbital (MO) energies (Koopmans' theorem (KT)) of a Hartree–Fock (HF) wavefunction. These values tend to overestimate experimental IPs because they neglect both electron correlation and relaxation of the remaining $N - 1$ electrons. Orbital assignments based upon KT values also occasionally give improper ordering relative to experiment. Inclusion of electron correlation through density function theory (DFT) is complicated by the uncertain meaning of the orbital energies. With the exception of the orbital energy of the HOMO (defined as the first vertical IP in exact DFT), the Kohn–Sham (KS) orbital energies have no physical meaning.³ Nonetheless, Baerends has shown that accurate IPs could be obtained by DFT using a response potential and densities from configuration interaction wavefunctions.⁴ IPs derived from the KS orbital energies obtained from widely available exchange–correlation functions underestimate experimental values by several electronvolts due to the incorrect asymptotic behavior of these functionals.⁴ Various scaling methods have been devised to allow interpretation of PES by shifting the DFT KT IPs to match the first IP or by calculating the $N - 1$ density separately to include relaxation effects.⁵ Because these scaled values are still based upon KT, it is possible that interpretations relying upon these values may also assign the orbitals incorrectly, although the ordering typically agrees with experiment.^{5,6}

Green's functions methods can calculate accurate theoretical IPs by explicitly including electron correlation and relaxation effects.^{7–10} The HF KT IPs are the poles of the matrix representation of the Hartree–Fock Green's function (eq 1), where ϵ is the diagonal matrix of the HF orbital energies. Dyson

$$G(E) = (E\mathbf{1} - \epsilon)^{-1} \quad (1)$$

showed that electron correlation and relaxation effects could be recovered through incorporation of an effective potential called the self-energy $\Sigma(E)$.¹¹ The exact IPs would then be the poles of the many-body Green's function (eq 2) if the exact self-energy was known. The approximate self-energy is calcu-

$$G(E) = (E\mathbf{1} - \epsilon - \Sigma(E))^{-1} \quad (2)$$

lated through various methods. Truncation of the infinite order expansion of $\Sigma(E)$ to second and third order are known as the 2ph- and extended 2ph-Tamm-Dancoff approximation (TDA), respectively. These methods provide an accurate and full ionization spectrum, including satellite and shakeup lines. However, full calculation of the ionization spectrum is often unnecessary, so a simplified method that omits diagonalization of certain matrices has been devised. The outer-valence Green's function (OVGF) method corresponds to the truncation of the self-energy to third order and tends to be highly accurate for the highest IPs of a system. The quasiparticle picture assumed within OVGf does not allow mixing of states in the ionized molecule and is inappropriate for inner valence IPs.

Green's functions methods have been used to analyze the electronic structure and bonding of various chemical systems,^{9b,12} including several of transition metal complexes.^{13,14} In this paper, we present OVGf IPs for a series of Mo and W complexes. Molecules of these metals are similar in structure but often exhibit significant differences in reactivity. The accuracy of GF methods presents a means of examining the underlying differ-

TABLE 1: Abbreviations for Basis Sets Used in This Study

| | M (M = Mo, W) | | C,O | | Cl |
|---|---|----------------|----------------|---|-------------------|
| A | M = Mo (5s5p4d1f)/[3s3p3d1f] M = W (5s6p4d1f)/[3s3p3d1f] | L ^a | TZVP | X | (4s4p1d)/[3s3p1d] |
| B | M = Mo (6s6p5d1f)/[4s4p4d1f] M = W (6s7p5d1f)/[4s4p4d1f] | M | TZVP+(s,p) | Y | (5s5p2d)/[4s4p2d] |
| C | M = Mo (7s7p6d2f)/[5s5p5d2f] M = W (7s8p6d2f)/[5s5p5d2f] | N | TZVP+(2s,2p,d) | Z | aug-cc-pvtz |
| D | M = Mo,W (8s7p6d2f1g)/[6s5p3d2f1g] | O | aug-cc-pvtz | | |

^a Basis set used for hydrogen atoms in basis set L was of TZV quality.

ences in electronic structure that result in the differences in reactivity. Five species of varying oxidation state and ligand sphere were selected: $M(\text{CO})_6$ (d^6 ; π -accepting ligands), $[\text{M}(\text{OCl}_4)]^-$ (d^1 ; π -donor ligands), $[\text{MO}_4]^-$ (d^0 ; π -donor ligands), and $M(\text{Me})_6$ and $M\text{H}_6$ (d^0 ; σ -donor ligands). OVGf IPs of these species generally are within ± 0.2 eV of available experimental vertical detachment energies. Within the data presented, the OVGf method fails for the inner valence MOs of the metal carbonyl complexes due to the coupling of excited states of the ion. Calculation of the IPs using the TDA gives results consistent with the experimental PES.

Theoretical Methods

Geometry optimizations were performed at the DFT/mPW1PW91¹⁵ level using Gaussian 03¹⁶ and the basis sets listed in Table 1. Molybdenum¹⁷ and tungsten¹⁸ were represented by the Ermler–Christiansen (EC) relativistic effective core potential (RECP) basis sets (A) with Couty and Hall's¹⁹ improved ($n + 1$)p contraction and augmented with one (B) and two (C) sets of diffuse (s, p, d) and polarization (f) functions. Additional calculations were performed using the Stuttgart-Bonn RECP (D) augmented with two f-type and one g-type set of polarization functions.²⁰ Carbon, oxygen, and hydrogen were represented with the Dunning split-valence triple- ζ plus polarization functions (TZVP) basis sets²¹ augmented as shown in Table 1. The Wadt–Hay RECP basis set²² for chlorine was augmented with one (X) and two (Y) sets of diffuse and polarization functions. Calculations were also performed using Dunning's augmented correlation-consistent triple- ζ basis sets.²³ Green's functions calculations were performed in Gaussian 03 (OVGF) and GAMESS-UK²⁴ (OVGF and 2ph-TDA) using the frozen-core approximation.

Results and Discussion

Theoretical geometries for all species are listed in Table 2a–d and agree well with known X-ray crystal structures.^{25,26} Theoretical vertical IPs (KT(HF), KT(DFT), P3, OVGf, TDA) and available experimental^{27–30} vertical detachment energies (VDEs) are listed in Tables 3–11 and correspond to the values reported in the experimental studies. Throughout the following discussion, VDE will refer to the experimental data and IP will reference the theoretical values. Orbital assignments are made on the basis of the orbital characters in the HF wavefunction and are listed in the tables in ascending order of OVGf IP. Pole strengths for OVGf IPs exceed 0.88 in most cases, meaning that less than 12% of the expected intensity of the line is borrowed from other states.^{7b} The partial third-order quasiparticle (P3) method omits certain third-order terms evaluated over four virtual MO indices.³¹ Although P3 has been reported to provide more accurate results than OVGf,^{10,32} this method tends to overestimate IPs for the species presented in this study. HF and DFT Koopmans' theorem values are included for contrast and have not been scaled or corrected. These correspond poorly

to experimental data due to their omission of electron relaxation and/or correlation effects. Comparison of the KT data in the tables shows that electron correlation included by DFT overcorrects versus HF by 1–3 eV.

[M(CO)₆]. The optimized geometries (Table 2a) of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are within 0.01 Å of experimental values.³³ Bond distances for the modified metal EC basis sets A–C do not vary significantly with addition of polarization and diffuse functions to the metal and ligands. These basis sets also give the correct ordering of the M–C bond distance (Mo > W). The Stuttgart RECP basis set gives similar C–O bond distances but predicts a longer M–C bond for $\text{W}(\text{CO})_6$. The theoretical IPs for basis set AL are listed in Table 3 and show good qualitative agreement with experimental photoelectron spectra.²⁴ The three bands observed below 17 eV were assigned^{25d} on the basis of Hillier and Saunders' ab initio calculation³⁴ of $\text{Cr}(\text{CO})_6$: the first VDE corresponds to the metal d-type t_{2g} MOs; the second to the t_{1u} M–C bonding MO (M $np + \sigma$ CO); and the broad third band (~ 14.0 – 16.6 eV) to the closely spaced e_g M–C bonding MO (M ($n - 1$) $d_{x^2-y^2}$, $d_{z^2} + \sigma$ CO) and the t_{1g} , t_{2g} , t_{1u} , and t_{2u} π CO MOs.

The errors in the OVGf IPs for the first VDE ($2t_{2g}$) are listed in Table 4 and vary with basis set and OVGf method. For $\text{Mo}(\text{CO})_6$, methods A and C provide the best estimates of the experimental VDE in smaller basis sets and method B consistently underestimates the magnitude of the IP. Augmentation of the EC basis set improves the OVGf estimate such that the method C value with basis set CO deviates from the reported value^{25d} by 0.06 eV. The Stuttgart ECP basis set (DO) also gives poor correlation in method B but is equivalent to the largest of the EC basis sets in methods A and C. Patterns in basis set and method dependence for $\text{W}(\text{CO})_6$ are similar to those obtained for the Mo analogue. Comparison of the data for $\text{W}(\text{CO})_6$ to experimental data is complicated by the spin–orbit splitting of the first VDE into U' and E'' (double group O^*) components separated by 0.26 eV.^{24d} The present OVGf calculations are nonrelativistic and do not incorporate spin–orbit coupling, but the results for the C method are in good agreement with the VDE assigned to the U' component.^{24d}

For higher IPs, the OVGf methods produce poor results in comparison to experiment due to the breakdown of the quasiparticle picture. The second IP corresponds well to the experimental VDE in smaller basis sets, but errors increase with basis set size. This increase in error is accompanied by a decrease in pole strength for this line (method B: AL, 0.882; CO, 0.874) indicating that mixing with other states is important even for the second IP. Theoretical estimates also predict the W second IP to be lower than that of Mo, whereas the experimental data show the second VDE for the W shifted to slightly higher energy.

The third broad band in the PES is assigned to the t_{1g} , t_{2g} , t_{1u} , and t_{2u} π CO bonding MOs and the M–C e_g bonding MO on the basis of previous theoretical interpretations. Of these,

TABLE 2

(a) Comparison of DFT Geometries for $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$) to Experimental Crystal Structures

| M | basis set | $d(\text{M}-\text{C})$ | $d(\text{C}=\text{O})$ |
|------------------|-----------|------------------------|------------------------|
| Mo | AL | 2.055 | 1.137 |
| | BM | 2.055 | 1.137 |
| | CN | 2.057 | 1.139 |
| | CO | 2.057 | 1.136 |
| | DO | 2.052 | 1.136 |
| exp ^a | | 2.063 | 1.145 |
| W | AL | 2.049 | 1.139 |
| | BM | 2.050 | 1.139 |
| | CN | 2.052 | 1.140 |
| | CO | 2.051 | 1.138 |
| | DO | 2.063 | 1.138 |
| exp ^a | | 2.058 | 1.148 |

(b) Comparison of DFT Geometries to Experimental X-ray Structures for $M(\text{Me})_6$ ($M = \text{Mo}, \text{W}$) in Basis Set BM

| M | $d(\text{M}-\text{C}_a)$ | $d(\text{M}-\text{C}_b)$ | $\angle(\text{C}_a-\text{M}-\text{C}_a)$ | $\angle(\text{C}_b-\text{M}-\text{C}_b)$ |
|------------------|--------------------------|--------------------------|--|--|
| Mo | 2.116 | 2.177 | 74.88 | 96.91 |
| exp ^b | 2.115 | 2.190 | 74.5 | 96.9 |
| W | 2.125 | 2.173 | 76.47 | 94.28 |
| exp ^c | 2.118 | 2.179 | 76.5 | 95.7 |

(c) Theoretical Geometries for $M\text{H}_6$ ($M = \text{Mo}, \text{W}$) at the DFT/mPW1PW91 Level in Basis Set CO

| M | | $d(\text{M}-\text{H}_1)$ | $d(\text{M}-\text{H}_2)$ | $\angle(\text{H}_1-\text{M}-\text{H}_2)$ |
|----|----------|--------------------------|--------------------------|--|
| Mo | C_{3v} | 1.631 | 1.683 | 35.55 |
| | C_{5v} | 1.649 | 1.712 | 116.57 |
| W | C_{3v} | 1.6494 | 1.6981 | 36.52 |
| | C_{5v} | 1.6657 | 1.7228 | 114.86 |

(d) Theoretical Geometries of $[\text{MCl}_4\text{O}]^-$ ($M = \text{Mo}, \text{W}$) at the DFT/mPW1PW91 Level in Various Basis Sets

| M | basis set | $d(\text{M}-\text{O})$ | $d(\text{M}-\text{Cl})$ | $\angle(\text{O}-\text{M}-\text{Cl})$ |
|------------------|-----------|------------------------|-------------------------|---------------------------------------|
| Mo | BMX | 1.640 | 2.360 | 105.38 |
| | BNY | 1.645 | 2.358 | 105.83 |
| | DOZ | 1.643 | 2.355 | 105.64 |
| exp ^d | | 1.645 | 2.342 | 103.72 |
| W | BMX | 1.669 | 2.357 | 105.35 |
| | BNY | 1.673 | 2.357 | 105.72 |

(e) Theoretical Geometries for $[\text{MO}_4]^-$ ($M = \text{Mo}, \text{W}$) at the DFT/mPW1PW91 and MP2 Levels in Various Basis Sets.

| M | basis sets | $d(\text{M}-\text{O}_a)$ | $d(\text{M}-\text{O}_b)$ | $\angle(\text{O}_a-\text{M}-\text{O}_a)$ | $\angle(\text{O}_b-\text{M}-\text{O}_b)$ |
|----|------------|--------------------------|--------------------------|--|--|
| Mo | BM | 1.725 | 1.818 | 97.8 | 111.1 |
| | CN | 1.730 | 1.819 | 97.6 | 111.1 |
| | BM (MP2) | 1.736 | 1.770 | 100.5 | 106.4 |
| | CN (MP2) | 1.752 | 1.777 | 99.7 | 106.4 |
| | DO | 1.721 | 1.813 | 97.9 | 111.0 |
| W | BM | 1.741 | 1.821 | 99.2 | 111.2 |
| | CN | 1.744 | 1.822 | 98.9 | 111.2 |
| | BM (MP2) | 1.761 | 1.799 | 99.5 | 108.6 |
| | CN (MP2) | 1.766 | 1.801 | 98.7 | 108.5 |
| | DO | 1.746 | 1.827 | 99.2 | 111.0 |

^a Reference 25 (X-ray structure). ^b Reference 36a. ^c Reference 36b. ^d Reference 26 (X-ray structure).

the third VDE in this band is assigned to the e_g orbital on the basis of relative intensities of the He I and He II experimental bands.^{24d} However, this MO corresponds to the first IP of the band in each OVGf method. Direct comparison of this IP to the assigned VDE gives reasonable results in small basis sets, but behavior in larger basis sets follows that shown for the second IP. The OVGf results for the remaining π CO MOs also correspond poorly to experiment (error >1 eV). These results are due to the breakdown of the quasiparticle picture as indicated by the polestrengths of the lines (0.78–0.82). A similar

case is shown for the analogue $\text{Cr}(\text{CO})_6$ where the first and second IPs are well-described by the quasiparticle picture, but coupling of 2h1p charge transfer (CT) states to the 1h states is significant for the π CO MOs.¹⁴

In the Mo and W complexes, the first IP is well described by the 1h picture, but for higher IPs, mixing of the 1h and 2h1p states through diagonalization of the relevant matrices of the self-energy is required to properly describe electron detachment. To address this issue, we have performed 2ph-TDA calculations in basis set AL to incorporate the CT effects. Table 5 lists the results of these calculations below 16 eV, which show very good agreement with the experimental PES. The breakdown of the quasiparticle picture for these molecules shows the danger of assigning PES based upon scaled Kohn–Sham orbital energies, which may result in incorrect assignment of the experimental VDEs. Surprisingly, scaled DFT KT IPs for these and related complexes correspond well to experiment,⁵ even in the region where the quasiparticle picture breaks down. However, it is possible given the uncertain physical meaning of the KS orbital energies, that this result is fortuitous.

$M(\text{Me})_6$. The photoelectron spectrum of hexamethyltungsten was reported by Green et al.²⁵ in the late 1970s prior to the discovery of its distorted structure.³⁵ As a result, the three lowest IPs were assigned originally to MOs in the assumed octahedral symmetry. The experimental He–I spectrum²⁵ for WMe_6 shows five bands below 16 eV; the two highest energy bands are broad and overlap. Green et al.'s interpretation of the PES assigned the first three VDEs to the t_{1u} , a_{1g} , and e_g W–C bonding orbitals, respectively, but their relative intensities did not fit those predicted on the basis of orbital degeneracy.

Geometries were optimized at the DFT(mPW1PW91)/AL level based upon the C_3 distorted trigonal prismatic structure determined by X-ray crystallography^{32b,36} and previous theoretical work.³⁷ Calculated bond lengths and angles (Table 2b) fall within 0.02 Å and 1.5° of experimental values obtained by X-ray crystallography. Theoretical IPs for WMe_6 and MoMe_6 are listed in Table 6 with experimental PES data (W only). The highest occupied MOs for this d^0 complex are the six M–C bonding orbitals which decompose as $2a + 2e$ in C_3 symmetry. The OVGf calculations assign the first three relatively sharp bands in the PES to ejection of electrons from the 12a, 11e, and 10e W–C bonding MOs with contributions from the 5d metal d AOs. The OVGf IP for the 11a W–C bonding MO (metal contribution from the 6s AO) corresponds to a shoulder at 11.55 eV in the 11.97 eV VDE. The 11.97 eV VDE and the broad band from ~13–15 eV are assigned to detachment from two sets of closely spaced C–H-bonding MOs (Table 5). The 9e and 10a IPs are assigned to the 11.97 band, and the remainder of the IPs listed in Table 4 make up the 13–15 eV band. The average errors for the three OVGf methods for the four well-defined VDEs in the experimental spectrum reported in Table 5 are less than 0.25 eV (the A and C methods give errors of ~0.14 eV). Including the 11a IP assigned to the 11.55 eV shoulder reduces this error to 0.18 eV for method B. An examination of the errors for the individual OVGf IPs shows that method A is the most consistent method (<0.15 eV) and method C gives the best correlation to experiment for the highest two M–C MOs and method B performs better for the lower two M–C MOs (10e and 9e).

Tables 2b and 6 also show the results of calculations on MoMe_6 for which only the X-ray structure is known.³⁸ OVGf predicts that the C–H-bonding MOs will be similar between the Mo and W analogues, but that the M–C bonding orbitals for Mo will be shifted to lower energies. In particular, the

TABLE 3: Theoretical Ionization Potentials (OVGF < 17 eV) for M(CO)₆ (M = Mo, W) in Basis Set AL

| M | symmetry | | KT | KT(DFT) | P3 | OVGF ^a | | | exp |
|----|------------------|---|-------|---------|-------|-------------------|-------|-------|-------|
| | | | | | | A | B | C | |
| Mo | 2t _{2g} | M d _{xy,xz,yz} | 9.06 | 7.30 | 8.85 | 7.96 | 7.47 | 8.14 | 8.50 |
| | 7t _{1u} | M p _{x,y,z} + σ CO | 16.26 | 11.88 | 14.34 | 13.75 | 13.41 | 13.88 | 13.32 |
| | 5e _g | M d _{x²-y²,z²} + σ CO | 17.99 | 13.60 | 16.12 | 15.33 | 14.94 | 15.45 | 14.66 |
| | 1t _{1g} | π CO | 17.51 | 13.33 | 15.77 | 15.44 | 15.41 | 15.52 | 14.18 |
| | 1t _{2u} | | 17.66 | 13.47 | 15.89 | 15.57 | 15.53 | 15.64 | 14.4 |
| | 6t _{1u} | | 17.94 | 13.67 | 16.15 | 15.77 | 15.70 | 15.86 | 15.2 |
| | 1t _{2g} | | 18.13 | 13.88 | 16.53 | 16.02 | 15.98 | 16.13 | 15.6 |
| W | 2t _{2g} | M d _{xy,xz,yz} | 8.91 | 7.29 | 8.47 | 8.05 | 7.59 | 8.17 | 8.56 |
| | 7t _{1u} | M p _{x,y,z} + σ CO | 16.49 | 12.06 | 14.54 | 13.90 | 13.59 | 14.03 | 13.27 |
| | 5e _g | M d _{x²-y²,z²} + σ CO | 18.37 | 13.83 | 16.48 | 15.58 | 15.23 | 15.71 | 14.88 |
| | 1t _{1g} | π CO | 17.52 | 13.32 | 15.73 | 15.33 | 15.31 | 15.42 | 14.20 |
| | 1t _{2u} | | 17.67 | 13.46 | 15.84 | 15.46 | 15.43 | 15.55 | 14.42 |
| | 6t _{1u} | | 18.02 | 13.70 | 16.16 | 15.70 | 15.62 | 15.80 | 15.2 |
| | 1t _{2g} | | 18.18 | 13.91 | 16.45 | 15.92 | 15.88 | 16.04 | 15.54 |

^a Pole strengths exceed 0.8.**TABLE 4: Comparison of the First and Second IPs Calculated by OVGF to Experiment for M(CO)₆ (M = Mo, W)^a**

| | Mo | | | W | | |
|----|--------------|--------------|--------------|--------------|--------------|--------------|
| | A | B | C | A | B | C |
| AL | 7.96 (0.46) | 7.47 (0.96) | 8.14 (0.28) | 8.05 (0.51) | 7.59 (0.97) | 8.17 (0.39) |
| | 13.75 (0.43) | 13.41 (0.09) | 13.88 (0.56) | 13.89 (0.62) | 13.59 (0.32) | 14.03 (0.76) |
| BM | 8.07 (0.35) | 7.58 (0.84) | 8.27 (0.15) | 8.02 (0.54) | 7.50 (1.06) | 8.12 (0.44) |
| | 13.77 (0.45) | 13.43 (0.11) | 13.91 (0.59) | 13.89 (0.62) | 13.57 (0.30) | 14.02 (0.75) |
| CN | 8.19 (0.23) | 7.95 (0.47) | 8.43 (0.01) | 8.20 (0.36) | 7.85 (0.71) | 8.36 (0.30) |
| | 13.89 (0.57) | 13.67 (0.35) | 14.06 (0.74) | 14.01 (0.74) | 13.78 (0.51) | 14.17 (0.90) |
| CO | 8.27 (0.15) | 8.11 (0.31) | 8.56 (0.14) | 8.28 (0.02) | 7.99 (0.57) | 8.49 (0.07) |
| | 13.99 (0.64) | 13.81 (0.49) | 14.20 (0.88) | 14.11 (0.84) | 13.91 (0.64) | 14.30 (1.03) |
| DO | 8.25 (0.17) | 7.85 (0.57) | 8.53 (0.11) | 8.24 (0.06) | 7.76 (0.80) | 8.41 (0.15) |
| | 13.91 (0.59) | 13.65 (0.33) | 14.11 (0.79) | 14.00 (0.73) | 13.73 (0.46) | 14.18 (0.91) |

^a Absolute error is listed in parentheses.**TABLE 5: Comparison of the IPs Calculated by TDA to Experiment for M(CO)₆ (M = Mo, W)**

| Mo(CO) ₆ | | W(CO) ₆ | |
|---------------------|------------------|--------------------|------------------|
| TDA | exp ^a | TDA | exp ^a |
| 7.86 | 8.50 | 7.77 | 8.56 |
| 13.40 | 13.32 | 13.49 | 13.27 |
| 13.72 | | 13.54 | |
| 14.17 | 14.18 | 14.06 | 14.20 |
| 14.62 | 14.4 | 14.50 | 14.42 |
| 14.63 | 14.66 | 14.74 | 14.88 |
| 15.00 | 15.2 | 14.94 | |
| 15.39 | | 15.08 | 15.2 |
| 15.40 | | 15.33 | 15.54 |
| 15.64 | 15.6 | 15.84 | |

^a Reference 27d.

MoMe₆ 11a MO with contributions from the metal s AO is predicted to be found 1.14 eV higher than that of WMe₆. This difference is consistent with the relativistic contraction of the 6s AO in W, which also results in an s²d⁴ ground state atomic electron configuration for W in comparison to the s¹d⁵ configuration of Cr and Mo. From these results, OVGF predicts MoMe₆ to have an additional peak in its PES as 11a should be well separated from the C–H VDE bands.

MH₆. Various groups have reported the non-octahedral geometries of d⁰ metal hexahydrides.³⁹ Ionization potentials have been calculated from the optimized geometries (Table 2c) of the lowest two MH₆ structures: the C_{3v} distorted trigonal prism and the C_{5v} pentagonal pyramid. These two structures are near degenerate, but the only the C_{3v} isomer of WH₆ has been observed through matrix isolation.⁴⁰ Group theory predicts that each of these structures will have four bands arising from the M–H-bonding MOs (C_{3v}, 2a₁ + 2e₁; C_{5v}, 2a₁ + e₁ + e₂). In C_{3v}

symmetry, the OVGF data (Table 7) show that these bands for each complex are arranged 3e < 4a₁ < 2e < 3a₁ with the IPs for WH₆ shifted to lower energies. For C_{5v}, the HOMO for each complex is the 1e₂ M–H-bonding MO. In MoH₆, the second and third IPs are 4a₁ and 2e₁, respectively, the opposite of W. For MoH₆, the second and third IPs are similar in energy and unlikely to be observed as separate bands, if the PES could be obtained. The W complex has each of these four IPs well separated, but shifted to lower energies compared to Mo. The fourth IP in each isomer is shifted to lower energies in W due to the relativistic contraction of the ns orbitals.

[MCl₄O]⁻. Wang et al.²⁶ have recently reported the photoelectron spectrum of [MoCl₄O]⁻ with an interpretation of the detachment order based upon scaled DFT orbital energies. Our DFT geometries for this species (Table 2d) are consistent with experiment and previous theoretical results. In Table 8, theoretical IPs are listed for the six highest α and five highly β occupied MOs in basis set ALX. The OVGF ordering of the MOs is consistent with Wang et al.'s earlier assignment with the unpaired electron located in the d_{xy} (2b₂) orbital. The remaining orbitals are ligand-based with contributions either in the plane (1a₂, 6e) or out of the plane (3b₁, 5e, 8a₁) of the chlorides. The α and β OVGF IPs for MOs of the same symmetry are separated by less than 0.2 eV, suggesting a small singlet–triplet gap for neutral MoCl₄O. This result is consistent with unrestricted DFT calculations of [Mo(edt)₂O]⁻ and comparisons between the PES of Mo(V) and V(V) complexes.²⁶ The small separation likely precludes observation of individual detachment energies for α and β spin orbitals. For this reason, the average of the α and β OVGF IPs are compared to the reported VDEs (Table 9).

TABLE 6: Theoretical Ionization Potentials for M(Me)₆ (M = Mo, W) in Basis Set BM

| M | symmetry | | KT | KT(DFT) | P3 | OVGF ^a | | | exp ^b | |
|-----|--------------------|--------------|-------|---------|-------|-------------------|-------|-------|------------------|------|
| | | | | | | A | B | C | | |
| Mo | 12a | σ M–C | 9.61 | 7.01 | 8.73 | 8.35 | 8.11 | 8.47 | | |
| | 11e | | 10.44 | 7.49 | 9.30 | 8.93 | 8.56 | 9.03 | | |
| | 10e | | 11.75 | 8.46 | 10.45 | 9.92 | 9.57 | 10.05 | | |
| | 11a | | 12.33 | 9.13 | 11.00 | 10.65 | 10.45 | 10.76 | | |
| | 9e | σ C–H | 13.67 | 9.95 | 12.48 | 12.09 | 12.14 | 12.23 | | |
| | 10a | | 13.81 | 10.10 | 12.62 | 12.27 | 12.33 | 12.40 | | |
| | 8e | | 14.86 | 11.06 | 13.63 | 13.25 | 13.29 | 13.38 | | |
| | 9a | | 14.97 | 11.20 | 13.74 | 13.40 | 13.46 | 13.52 | | |
| | 7e | | 15.23 | 11.39 | 13.94 | 13.54 | 13.56 | 13.67 | | |
| | 8a | | 15.24 | 11.37 | 13.97 | 13.60 | 13.65 | 13.73 | | |
| | 6e | | 15.92 | 12.01 | 14.62 | 14.26 | 14.28 | 14.37 | | |
| | 7a | 16.74 | 12.67 | 15.35 | 14.96 | 14.99 | 15.07 | | | |
| | W | 12a | | 9.81 | 7.03 | 8.82 | 8.50 | 8.35 | 8.61 | 8.59 |
| | | 11e | | 10.65 | 7.64 | 9.52 | 9.19 | 8.99 | 9.30 | 9.33 |
| 10e | | | 12.01 | 8.66 | 10.67 | 10.30 | 10.09 | 10.41 | 10.17 | |
| 11a | | | 13.43 | 9.92 | 12.05 | 11.71 | 11.57 | 11.81 | c | |
| 9e | | | 13.61 | 9.94 | 12.47 | 12.12 | 12.19 | 12.26 | 11.97 | |
| 10a | | | 13.73 | 10.09 | 12.61 | 12.29 | 12.36 | 12.42 | d | |
| 8e | | | 14.84 | 11.06 | 13.65 | 13.31 | 13.35 | 13.43 | e | |
| 9a | | | 14.89 | 11.13 | 13.70 | 13.41 | 13.46 | 13.52 | e | |
| 7e | | | 15.14 | 11.32 | 13.90 | 13.56 | 13.60 | 13.68 | e | |
| 8a | | | 15.22 | 11.35 | 13.98 | 13.64 | 13.69 | 13.76 | e | |
| 6e | | 15.86 | 12.00 | 14.64 | 14.32 | 14.35 | 14.43 | e | | |
| 7a | | 16.63 | 12.63 | 15.34 | 14.99 | 15.03 | 15.10 | e | | |
| | error ^f | | | | 0.13 | 0.22 | 0.14 | | | |

^a Pole strengths exceed 0.88. ^b Reference 28. ^c This band may correspond to a shoulder observed at 11.55 eV. ^d Assigned to the 11.9 eV band. ^e These IPs are assigned to a broad peak ranging from 12.5 to 15.0. ^f Mean absolute error calculated from the four well-defined experimental VDEs.

TABLE 7: Theoretical Ionization Potentials for MH₆ (M = Mo, W) in Basis Set CO

| M | symmetry | KT | KT(DFT) | P3 | OVGF ^a | | | |
|----|-----------------|-----------------|---------|-------|-------------------|-------|-------|-------|
| | | | | | A | B | C | |
| Mo | C_{3v} | 3e | 11.62 | 8.31 | 11.16 | 10.65 | 10.54 | 10.83 |
| | | 4a ₁ | 12.28 | 9.26 | 12.04 | 11.68 | 11.69 | 11.84 |
| | | 2e | 12.87 | 9.57 | 12.36 | 12.04 | 12.04 | 12.17 |
| | C_{5v} | 3a ₁ | 15.38 | 11.59 | 14.33 | 14.21 | 14.18 | 14.27 |
| | | 1e ₂ | 11.59 | 8.39 | 11.22 | 10.69 | 10.60 | 10.88 |
| | | 4a ₁ | 13.12 | 9.73 | 12.53 | 12.19 | 12.16 | 12.31 |
| | | 2e ₁ | 13.02 | 9.71 | 12.47 | 12.17 | 12.12 | 12.31 |
| W | C_{3v} | 3a ₁ | 15.02 | 11.33 | 14.05 | 13.90 | 13.88 | 13.98 |
| | | 3e | 11.78 | 8.57 | 11.24 | 11.00 | 10.95 | 11.12 |
| | | 4a ₁ | 12.49 | 9.35 | 12.06 | 11.84 | 11.86 | 11.96 |
| | C_{5v} | 2e | 13.04 | 9.62 | 12.38 | 12.16 | 12.17 | 12.27 |
| | | 3a ₁ | 16.12 | 12.18 | 15.03 | 14.90 | 14.90 | 14.97 |
| | | 1e ₂ | 11.56 | 8.45 | 11.14 | 10.84 | 10.81 | 10.98 |
| | | 2e ₁ | 12.99 | 9.64 | 12.36 | 12.17 | 12.18 | 12.27 |
| | 4a ₁ | 13.57 | 9.99 | 12.82 | 12.62 | 12.59 | 12.71 | |
| | 3a ₁ | 15.94 | 12.06 | 14.91 | 14.77 | 14.77 | 14.85 | |

^a Pole strengths for all reported IPs exceed 0.88.

Additionally, the OVGF IPs for 6e and 3b₂, separated by less than 0.1 eV were combined for comparison to the experimental VDEs.

On the basis of this averaging scheme, the experimental VDEs are assigned as first (2b₂), second (1a₂), third (3b₁, 6e), fourth (5e), and fifth (8a₁), identical to the assignment based upon scaled DFT.²⁶ OVGF method B gives the best overall correspondence to the experimental PES with an average 0.16 error for the basis sets reported in Table 9. The A and C methods give good results for the second, third, and fourth IPs but have errors exceeding 0.5 eV for the HOMO. The highest four IPs (B OVGF) show less than 0.1 eV deviation except for the fifth IP where the error exceeds the VDE by 5–7% due to contribution from shakeup states.²⁸ Tables 8 and 9 also include IPs for [WCl₄O][−] for which experimental data have not been reported. The predicted ordering of IPs according to OVGF is the same as for the Mo analogue, but removal of an electron

from the singly occupied d_{xy} MO (2b₂) is 1.2 eV lower for [WCl₄O][−]. Detachment of electrons from the ligand-based orbitals requires slightly more energy than the Mo species.

[MO₄][−]. Zhai et al. reported the PES of [MO₄][−] species in a larger discussion of group VIB oxides.³⁰ Three VDEs were observed for each complex and assigned on the basis of corrected DFT IPs (W only). Zhai et al. assigned the first VDE to detachment of either the α or β electron from the 6b₂ orbital, the second from the 2a₂ and 10 a₁ β MOs, and the third from the 5b₁ β MO. (Neutral MO₄ has a triplet ground state, so detachment of β electrons is generally preferred.) A similar interpretation may be made on the basis of the DFT KT IPs listed for WO₄[−] in Table 10.

Although the DFT geometries obtained in this study (Table 2e) are similar to those reported by Zhai et al., an interpretation of the PES based upon the OVGF IPs provide an alternate assignment of the VDEs. The first six α and five β OVGF IPs in basis set BM (DFT) are listed in Table 10. The first IP in each OVGF method is due to the 10a₁ β MO. Detachment from the α or β 6b₂ and the β 2a₂ spin MOs are similar in energy and may be combined into one line for comparison to the second VDE. The third IP would then be assigned to the β 5b₁ MO. Smaller basis sets sometimes reverse the order of the second and third IP. Average absolute errors for these assignments listed in Table 11 have been determined on the basis of the OVGF method with the best fit to experiment and are less than 0.2 eV. Generally for these species, method B provides data with much larger error than methods A and C. The average absolute errors for [MoO₄][−] exceed that of the W analogue due to the poor correlation of the first IP to the VDE. Unlike most other examples in this study, the P3 IP for this line corresponds well to experiment.

Geometries were also calculated at the MP2 level due to large errors in the first IP for the Mo species. The MP2 optimized geometries had the same symmetry (C_{2v}) and electronic state as the DFT geometries but gave shorter M–O_b bond lengths. Assignment of the spectrum from these geometries gives the

TABLE 8: Theoretical Ionization Potentials for $[\text{MCl}_4\text{O}]^-$ ($\text{M} = \text{Mo}, \text{W}$) in Basis Set BMX

| M | symmetry | KT_α (HF) | KT_α (DFT) | P3_α | OVGF $_\alpha^a$ | | | KT_β (HF) | KT_β (DFT) | P3_β | OVGF $_\beta^a$ | | |
|----|-----------------|-------------------------|--------------------------|--------------------|------------------|------|------|------------------------|-------------------------|-------------------|-----------------|------|------|
| | | | | | A | B | C | | | | A | B | C |
| Mo | 2b ₁ | 7.71 | 3.29 | 5.37 | 5.15 | 4.65 | 5.19 | | | | | | |
| | 1a ₂ | 7.37 | 4.17 | 6.27 | 6.05 | 6.09 | 6.15 | 7.12 | 4.01 | 6.05 | 5.88 | 5.89 | 5.96 |
| | 6e | 7.97 | 4.82 | 6.97 | 6.73 | 6.74 | 6.82 | 7.89 | 4.69 | 6.74 | 6.58 | 6.54 | 6.65 |
| | 3b ₂ | 8.00 | 4.82 | 6.90 | 6.74 | 6.73 | 6.81 | 7.97 | 4.82 | 6.86 | 6.70 | 6.69 | 6.77 |
| | 5e | 8.33 | 5.16 | 7.29 | 7.10 | 7.09 | 7.17 | 8.48 | 5.16 | 7.39 | 7.18 | 7.18 | 7.27 |
| W | 8a ₁ | 9.10 | 5.71 | 8.03 | 7.80 | 7.80 | 7.88 | 9.12 | 5.71 | 8.00 | 7.79 | 7.77 | 7.87 |
| | 2b ₂ | 6.62 | 2.46 | 4.09 | 4.03 | 3.48 | 4.04 | | | | | | |
| | 1a ₂ | 7.55 | 4.23 | 6.28 | 6.15 | 6.15 | 6.21 | 7.29 | 4.07 | 6.07 | 5.97 | 5.94 | 6.02 |
| | 3b ₁ | 8.15 | 4.89 | 6.89 | 6.81 | 6.76 | 6.85 | 8.14 | 4.88 | 6.87 | 6.79 | 6.74 | 6.83 |
| | 6e | 8.15 | 4.87 | 7.02 | 6.83 | 6.82 | 6.90 | 8.04 | 4.75 | 6.76 | 6.67 | 6.60 | 6.71 |
| | 5e | 8.46 | 5.18 | 7.28 | 7.14 | 7.10 | 7.19 | 8.57 | 5.19 | 7.38 | 7.22 | 7.19 | 7.28 |
| | 8a ₁ | 9.29 | 5.80 | 8.07 | 7.90 | 7.86 | 7.97 | 9.30 | 5.79 | 8.04 | 7.89 | 7.84 | 7.95 |

^a Pole strengths for all reported IPs exceed 0.9.**TABLE 9: Comparison between the OVGF IPs and Experimental VDEs for $[\text{MCl}_4\text{O}]^-$ ($\text{M} = \text{Mo}, \text{W}$)^a**

| M | | BMX | | | CNY | | | DOZ | | | exp ^b |
|--------------------|----------------------|------|------|------|------|------|------|------|------|------|------------------|
| | | A | B | C | A | B | C | A | B | C | |
| Mo | 2b ₂ | 5.20 | 4.68 | 5.22 | 5.15 | 4.65 | 5.19 | 5.21 | 4.58 | 5.26 | 4.68 X |
| | 1a ₂ | 5.93 | 5.90 | 5.99 | 5.96 | 5.99 | 6.06 | 6.09 | 6.07 | 6.18 | 6.00 A |
| | 3b ₁ + 6e | 6.62 | 6.56 | 6.67 | 6.69 | 6.68 | 6.76 | 6.78 | 6.70 | 6.84 | 6.76 B |
| | 5e | 7.07 | 7.01 | 7.12 | 7.14 | 7.13 | 7.22 | 7.22 | 7.16 | 7.30 | 7.08 C |
| | 8a ₁ | 7.73 | 7.66 | 7.78 | 7.79 | 7.78 | 7.88 | 7.84 | 7.77 | 7.92 | 7.23 D |
| error ^c | | 0.25 | 0.16 | 0.25 | 0.24 | 0.15 | 0.27 | 0.28 | 0.17 | 0.35 | |
| W | 2b ₂ | 4.03 | 3.48 | 4.04 | 4.06 | 3.56 | 4.10 | | | | |
| | 1a ₂ | 6.39 | 6.35 | 6.44 | 6.45 | 6.46 | 6.53 | | | | |
| | 3b ₁ + 6e | 6.78 | 6.73 | 6.82 | 6.84 | 6.86 | 6.93 | | | | |
| | 5e | 7.18 | 7.14 | 7.24 | 7.25 | 7.28 | 7.35 | | | | |
| | 8a ₁ | 7.90 | 7.85 | 7.96 | 7.97 | 7.98 | 8.06 | | | | |

^a See text for details. ^b Reference 29. ^c Mean absolute error.**TABLE 10: Theoretical Ionization Potentials for $[\text{MO}_4]^-$ ($\text{M} = \text{Mo}, \text{W}$) in Basis Set BM**

| M | symm | KT_α (HF) | KT_α (DFT) | P3_α | OVGF $_\alpha^a$ | | | KT_β (HF) | KT_β (DFT) | P3_β | OVGF $_\beta^a$ | | | |
|----|------------------|-------------------------|--------------------------|--------------------|------------------|------|------|------------------------|-------------------------|-------------------|-----------------|------|------|------|
| | | | | | A | B | C | | | | A | B | C | |
| Mo | 6b ₂ | 7.32 | 3.64 | 8.22 | 6.02 | 6.47 | 6.15 | | | | | | | |
| | 6b ₁ | 7.89 | 4.22 | 8.10 | 6.48 | 6.76 | 6.63 | 10a ₁ | 5.97 | 3.67 | 5.43 | 4.79 | 4.57 | 4.96 |
| | 2a ₂ | 8.41 | 4.19 | 8.12 | 6.69 | 6.85 | 6.84 | 2a ₂ | 7.54 | 3.81 | 6.91 | 5.91 | 5.99 | 6.06 |
| | 10a ₁ | 8.29 | 4.57 | 8.66 | 6.80 | 7.10 | 6.94 | 6b ₂ | 7.26 | 3.65 | 8.15 | 6.00 | 6.45 | 6.13 |
| | 5b ₂ | 9.23 | 4.61 | 8.44 | 7.07 | 7.11 | 7.21 | 5b ₁ | 7.33 | 4.13 | 7.44 | 6.16 | 6.40 | 6.33 |
| W | 9a ₁ | 9.96 | 5.45 | 9.73 | 7.97 | 8.11 | 8.09 | 5b ₂ | 8.51 | 4.27 | 7.33 | 6.33 | 6.30 | 6.48 |
| | 6b ₂ | 7.34 | 3.59 | 7.76 | 6.35 | 6.14 | 5.98 | | | | | | | |
| | 6b ₁ | 7.99 | 4.25 | 7.98 | 6.81 | 6.73 | 6.56 | 10a ₁ | 5.76 | 3.81 | 5.60 | 5.29 | 5.13 | 5.43 |
| | 2a ₂ | 8.36 | 4.19 | 7.93 | 6.82 | 6.82 | 6.65 | 2a ₂ | 7.28 | 3.81 | 7.66 | 5.92 | 6.30 | 6.09 |
| | 10a ₁ | 8.57 | 4.60 | 8.65 | 7.25 | 7.13 | 6.97 | 6b ₂ | 7.58 | 3.56 | 6.97 | 5.95 | 6.08 | 6.12 |
| | 5b ₂ | 9.26 | 4.67 | 8.49 | 7.22 | 7.26 | 7.11 | 5b ₁ | 7.61 | 4.14 | 7.53 | 6.34 | 6.57 | 6.52 |
| | 9a ₁ | 10.32 | 5.86 | 10.24 | 8.65 | 8.56 | 8.43 | 5b ₂ | 8.60 | 4.38 | 7.59 | 6.48 | 6.53 | 6.64 |

^a Pole strengths for all reported IPs exceed 0.9.**TABLE 11: Comparison with OVGF IPs and Experimental VDEs for $[\text{MO}_4]^-$ ($\text{M} = \text{Mo}, \text{W}$)**

| M | geometry | BM | CN | DO | exp ^a | |
|-------|---------------------------------|---|--------|--------|------------------|------|
| Mo | DFT | β 10a ₁ | 4.96 C | 5.04 C | 5.13 C | 5.45 |
| | | α, β 6b ₂ ; β 2a ₂ | 6.01 A | 6.05 A | 6.06 A | 5.82 |
| | | β 5b ₁ | 5.91 A | 5.97 A | 6.26 A | 6.02 |
| | error | | 0.20 | 0.20 | 0.27 | |
| | MP2 | β 10a ₁ | 5.22 C | 5.32 C | | |
| W | DFT | β 10a ₁ | 5.43 C | 5.53 C | 5.54 C | 5.44 |
| | | α, β 6b ₂ ; β 2a ₂ | 5.95 A | 5.99 A | 6.04 A | 5.88 |
| | | β 5b ₁ | 6.34 A | 6.38 C | 6.17 A | 6.24 |
| | error | | 0.08 | 0.09 | 0.12 | |
| | MP2 | β 10a ₁ | 5.44 A | 5.50 A | | |
| | α, β 6b ₂ | 5.80 A | 5.86 A | | | |
| | β 2a ₂ | 6.23 A | 6.22 C | | | |
| error | | 0.01 | 0.04 | | | |

^a Reference 30.

same first IP as for the DFT geometries. The second IP corresponds to detachment of an α or β electron from the 6b₂ MO and the third IP is the β 2a₂ MO. The errors for these assignments were also determined by the OVGF method with the best fit to experiment and are lower than those obtained from the DFT geometries (<0.1 eV average absolute error).

Conclusions

Theoretical IPs have been calculated for several Mo and W complexes using electron propagator methods. Ejection of electrons in purely ligand-based MOs (CO, CH) are similar for complexes of the two metals, but removal of electrons in metal d MOs in $[\text{MOCl}_4]^-$ requires more energetic photons for Mo than for W. Electrons in metal–ligand bonding MOs are more difficult to remove in W complexes, an observation consistent with the higher reduction potential for tungstate versus molybdate. Relativistic effects lower the IPs for MOs relative to Mo with significant contribution from the W 6s AO.

Comparison of these results to available PES shows that the VDEs can be calculated within ± 0.2 eV. However, the OVGf method breaks down for inner valence MOs where the ion states are not well described by a single reference state. Incorporation of the coupling of charge transfer states to the one-hole state through full diagonalization of the approximate self-energy in the TDA well represents the PES. The breakdown of the quasiparticle picture in the metal carbonyls reveals the danger in using one-particle methods including KT (HF) and KT(DFT) for the assignment of PES where CT states are likely to contribute. For well-behaved systems, use of scaled DFT KT IPs agrees with the OVGf values, but in some cases the assignment of IPs to orbitals differs because relaxation is directly determined by Green's function methods (as in the case of $[\text{MO}_4]^-$).

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