

A Theoretical Revisit to the Lowest Ionization Potentials in Metal–Metal Bonds

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Quadruply bonded complexes impart many characteristic features to structures, physical properties, and reactivity and have received continuous attention over the past four decades. These compounds are often composed of dinuclear metal centers of the group VI and VII elements. Among them, di-rhenium $[\text{Re}_2\text{Cl}_8]^{2-}$ was the first complex^[1] discovered with a formal bond order (FBO) of four, and the quadruply bonded di-molybdenum complexes have been the most abundantly characterized.^[2] The $\sigma^2\pi^4\delta^2$ motif of quadruple bonds was confirmed in a study^[3] reported in 2000 wherein a photodetachment experiment on the gaseous ion of $[\text{Re}_2\text{Cl}_8]^{2-}$ revealed the distinct resolution of three spectral detachment bands corresponding to the δ , π , and σ ionizations. Such photoionization techniques are an important experimental strategy to probe the electronic structure of multiple bonds.

Although photoionization experiments performed on multiply bonded complexes usually reveal more elaborate information, quantum mechanical (QM) calculations can provide theoretical insight into the molecular orbitals (MO) that determine the bonding schemes, and can elucidate geometric, energetic, and spectroscopic information. In addition to the single-configuration self-consistent field (SCF) theory and the SCF- $X\alpha$ scattered wave^[4] (SCF- $X\alpha$ -SW) analyses that are frequently referenced, recent studies have focused on density functional theories^[5] (DFT) and multi-configuration SCF (MCSCF,^[6] or complete active space SCF, CASSCF^[7]) methods. Owing to the balance between accuracy and efficiency, ab initio methods are frequently employed with simplified structural models^[8] using smaller basis sets, whereas DFT studies could, depending on the molecular size and properties of interest, take advantage of either authentic structures^[9] or geometrical simplifications.^[10] Choices of basis sets are thus more flexible in DFT runs. In spectral

computations, the aforementioned ionization energies (IEs) can be treated as the Franck–Condon process^[11] between the molecular ground state and its cationic states, and can then be evaluated by QM computations.

The quadruply bonded $\text{M}_2(\text{hpp})_4$ system^[12] ($\text{M} = \text{Cr}, \text{Mo}$, and W ; hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine; Figure 1) reported by Cotton

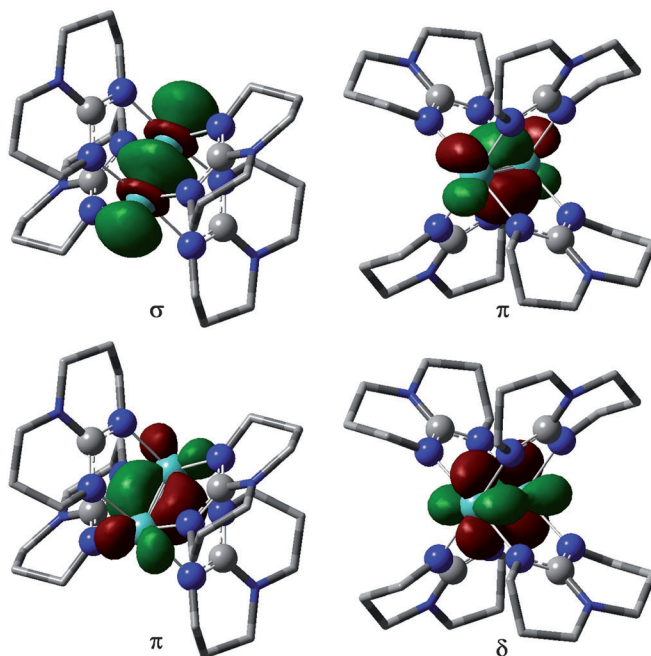


Figure 1. The structural motif of $\text{M}_2(\text{hpp})_4$ ($\text{M} = \text{Cr}, \text{Mo}$, and W , colored in cyan; N in blue and C in grey; hydrogen atoms omitted) as well as the four bonding orbitals between the M–M core.

et al., is one challenging exemplar. This coordination motif is computationally demanding because of the unique hpp ligand, which consists of bicyclic guanidates, leading to difficult structural simplification during calculations of the molecular properties. Moreover, these complexes exhibit extremely low ionization potentials^[12b] (IPs) relative to all of the compounds for which ionization data have been experimentally measured. Of particular interest is the $\text{W}_2(\text{hpp})_4$ molecule, which has an even lower first IE (3.51 eV onset, 3.78 eV vertical) than that of atomic cesium (3.89 eV). Cesium is known as the most readily ionized element across the periodic table.

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The factor that decreases the first IE in $W_2(\text{hpp})_4$ has been attributed to the filled-filled interaction between the W_2^{4+} δ orbital and the π orbitals of the anionic hpp that are appropriate in symmetry, contributing to the increase in the energy of its HOMO.^[13] Hybrid DFT computation on this δ ionization by Koopmans' theorem^[14] (KT) through the removal of an electron from the δ orbital resulted in a theoretical estimate of 3.57 eV.^[12b] Although this value lies in the onset IE, it does not include relativistic effects, and successive ionizations cannot be assigned using single-reference theories. The influence of relativistic effects in the structural chemistry of heavy elements was reviewed in detail by Pyykkö^[15] as well as more recently by Schwerdtfeger,^[16] several earlier studies^[17] also pointed out that without relativistic calculations the excited states could be reversed, and the deviation in IE could be significant.

In this study, the IPs of $Mo_2(\text{hpp})_4$ and $W_2(\text{hpp})_4$ were re-investigated with high-level multi-reference (MR) theories using the authentic structures to accurately analyze these atypical low IEs and to make further spectral assignments for the subsequent ionizations. Two series of effective core potential (ECP) basis sets of triple- ζ quality, in terms of LanL2TZ^[18] and Def2-TZVP,^[19] were used. An all-electron (AE) implementation of basis set developed for the third transition series (Hf-Hg), namely the segmented all-electron relativistically contracted (SARC) basis set,^[20] was exclusively used to include the Douglas-Kroll-Hess (DKH) relativistic correction^[21] for tungsten. Molecular symmetry (C_{2h}) was imposed during all computations. A simplified model of M_2L_4 ($M=Mo$ and W ; $L=(NH)_2CNH_2$; molecular structure shown in the Supporting Information, Figure S1) was intentionally created to assist orbital selection in the multi-configuration CASSCF computation at the initial stage and to compare the results with full molecular calculations.

The DFT (BP86)^[22] optimized interatomic distances of both M_2L_4 and $M_2(\text{hpp})_4$ agree well with the X-ray data (briefed in Table 1, with complete coordinates listed in Supporting Information Table S1). The computed first IE corresponding to ionization from the δ orbital (HOMO, A_g symmetry) for the Mo_2L_4 model is 4.109 eV at CASSCF/LanL2TZ, whereas the larger basis set of Def2-TZVP yields 3.965 eV. Three following ionizations corresponding to excitations from HOMO-1, HOMO-2, and HOMO-3 are 6.505 eV (σ orbital, A_g), 6.587 eV (π orbital, A_u), and 6.601 eV (π orbital, B_u) at the level of CASSCF/LanL2TZ;

Table 1. Fully optimized authentic geometries of $Mo_2(\text{hpp})_4$ and $W_2(\text{hpp})_4$ by DFT.^[a]

Complex	Bond Length [Å]				
	M–M	Longest M–N	Shortest M–N	Average M–N	
$Mo_2(\text{hpp})_4$	Exptl. ^[12a]	2.067	2.150	2.167	2.158
	DFT	2.084	2.160	2.163	2.162
$W_2(\text{hpp})_4$	Exptl. ^[12b]	2.162	–	–	2.129
	DFT	2.185	2.150	2.155	2.153

[a] BP86/Def2-TZVP.

at the CASSCF/Def2-TZVP level these values are 6.301, 6.380, and 6.396 eV, respectively. The deviation in IE due to different basis sets is ~ 0.2 eV, and is quite consistent in each excitation. In addition, CASSCF theory proposes that the one σ orbital and two π orbitals are nearly degenerate in the Mo_2L_4 model; therefore, we inevitably must reconfirm its correctness by using the authentic $Mo_2(\text{hpp})_4$ molecule. At the level of CASSCF/LanL2TZ the four IEs of $Mo_2(\text{hpp})_4$ are evaluated as 3.631 eV (δ), 6.033 eV (σ), 6.206 eV (π , A_u), and 6.210 eV (π , B_u).

Higher-level electronic correlation methods are therefore necessary to obtain more reliable figures, and multi-reference configuration interaction (MRCI) theory^[23] based on the converged CASSCF wavefunction was employed to correlate CASSCF IEs for both Mo_2L_4 and $Mo_2(\text{hpp})_4$. MRCI improved the first IE (δ) of the Mo_2L_4 model and authentic $Mo_2(\text{hpp})_4$ to 4.389 and 4.376 eV, respectively, in very good agreement with the experimental vertical IE of 4.33 eV. Although the CASSCF orbital diagram of $Mo_2(\text{hpp})_4$ indicates that HOMO-1, HOMO-2, and HOMO-3 are almost degenerate (Supporting Information, Figure S2), MRCI correlation was able to resolve the energetic levels between the σ and π ionizations corresponding to the other three Mo–Mo bonding orbitals. It therefore refined the three successive IEs of the $Mo_2(\text{hpp})_4$ molecule to 6.768 eV (σ), 7.033 eV (π , A_u), and 7.039 eV (π , B_u). These ionizations are located outside the experimental spectra with reference to the helium self-ionization peak (4.99 eV) and are not demonstrated in the photoionization picture.^[12b] The IEs of the four Mo–Mo bonding orbitals of Mo_2L_4 and $Mo_2(\text{hpp})_4$ are summarized in Table 2 and detailed in Supporting Information Tables S2 and S3. Interestingly, at the level of MRCI/LanL2TZ the IEs are improved only by a few tens of meV using $Mo_2(\text{hpp})_4$ compared with the model of Mo_2L_4 .

Table 2. Ionization energies of Mo_2L_4 and $Mo_2(\text{hpp})_4$ from the Mo–Mo orbitals, computed using MR theories with LanL2TZ^[a] and Def2-TZVP basis sets.

Ionization	IE [eV]			
	δ (A_g) ^[b]	σ (A_g)	π (A_u)	π (B_u)
CASSCF/LanL2TZ, Mo_2L_4	4.109	6.505	6.587	6.601
MRCI/LanL2TZ, Mo_2L_4	4.389	6.785	6.947	6.959
CASSCF/Def2-TZVP, Mo_2L_4	3.965	6.301	6.380	6.396
MRCI/Def2-TZVP, Mo_2L_4	4.506	6.909	7.048	7.062
CASSCF/LanL2TZ, $Mo_2(\text{hpp})_4$	3.631	6.033	6.206	6.210
MRCI/LanL2TZ, $Mo_2(\text{hpp})_4$	4.376	6.768	7.033	7.039

[a] The 6-311G(d,p) basis set is applied for H, C, and N. [b] Experimental onset IE is 4.01 eV and vertical IE is 4.33 eV, whereas DFT gave 3.85 eV according to reference [12b].

For the tungsten compounds in which the relativistic effect plays an important role, DKH correction up to the fourth order is applied in the MR computations with the SARC basis set. Starting with the W_2L_4 model, the use of the CASSCF wavefunction with the ECP basis sets of LanL2TZ and Def2-TZVP resulted in the first IE (δ) of 2.841 and 2.823 eV, respectively, whereas the SARC basis set gives 2.768 and 3.724 eV, respectively, with and without

second-order DKH (DKH2) correction. The fourth-order DKH (DKH4) result shows that the IE is almost converged out (2.765 eV), which suggests that higher-order terms can be neglected. Comparisons of subsequent IEs of W_2L_4 using these various basis sets at the CASSCF level are detailed in Supporting Information Table S4. For the authentic compound $W_2(hpp)_2$, CASSCF theory also significantly underestimates the δ ionization at 2.365 eV (LanL2TZ), 2.329 eV (SARC DKH2), and 2.326 eV (SARC DKH4), noting that the experimental peak appears beyond 3.514 eV.

Electronic correlation using MRCI on top of the CASSCF wavefunction appreciably improves the computed IEs of $W_2(hpp)_4$ and shows superior agreement to the experimental data. At the DKH2 level, MRCI/SARC generates the four IEs of interest for $W_2(hpp)_4$ at 3.594 eV (δ , A_g), 6.223 eV (π , A_u), 6.241 eV (π , B_u), and 6.842 eV (σ , A_g), while the DKH4 correction brings about an energetic difference of <0.004 eV in each excitation (Table 3, with a more detailed version available in Table S5, Supporting Information). Furthermore, theoretical computation for these IEs discloses distinct trends: for $Mo_2(hpp)_4$ the energetic sequence is $IE_\delta < IE_\sigma < IE_\pi$, while in the $W_2(hpp)_4$ system the order of IE_σ and IE_π is ranked as $IE_\delta < IE_\pi < IE_\sigma$. This reversal may be due to the σ orbital being formed by the overlap of $d_z^2-d_z^2$, and as the relativistic effect shows considerable impact in the third transition series, the electrons in the σ orbital of $W_2(hpp)_4$ experience more attraction from the tungsten nucleus and are therefore ionized with greater difficulty, rendering IE_σ the highest among all four metal–metal bonding orbitals. On the other hand, the error in the non-relativistic MRCI calculation for the IE_δ of $W_2(hpp)_4$ is

Table 3. Ionization energies for $W_2(hpp)_4$ from the W–W orbitals, computed using MR theories with LanL2TZ and SARC basis sets,^[a] with and without relativistic corrections.

Ionization	IE [eV]			
	δ (A_g) ^[b]	π (A_u)	π (B_u)	σ (A_g)
CASSCF/LanL2TZ	2.365	4.978	4.984	5.703
CASSCF/SARC DKH2	2.329	4.885	4.899	5.554
CASSCF/SARC DKH4	2.326	4.882	4.896	5.558
MRCI/LanL2TZ	3.431	6.077	6.081	6.756
MRCI/SARC non-relativistic	4.447	7.109	7.129	6.870
MRCI/SARC DKH2	3.594	6.223	6.241	6.842
MRCI/SARC DKH4	3.592	6.220	6.238	6.846

[a] The 6-311G(d,p) basis set is applied for H, C, and N. [b] Experimental onset IE is 3.514 eV and vertical IE is 3.76 eV; DFT gave 3.57 eV according to reference [12b].

~ 0.69 eV higher than the experimental vertical IE, and the two subsequent IE_π states are flipped above the cationizations from the δ and σ orbitals.

Both the DKH correction and the ECP approach yield consistent ionization sequences and reliable assignments to the photoelectron spectra of $W_2(hpp)_4$.^[13] The δ ionization has been undoubtedly indicated by the rightmost peak at 3.76 eV^[12b] (see also Figure 16.45 in reference [13]). The σ ionization falls on the peak at ~ 6.7 eV,^[13] and the shoulder at 6.0 eV^[13] could correspond to the two degenerate π ionizations. According to the orbital diagram in Figure 2, the energy gap of 7.67 eV between the δ and δ^* orbitals can be

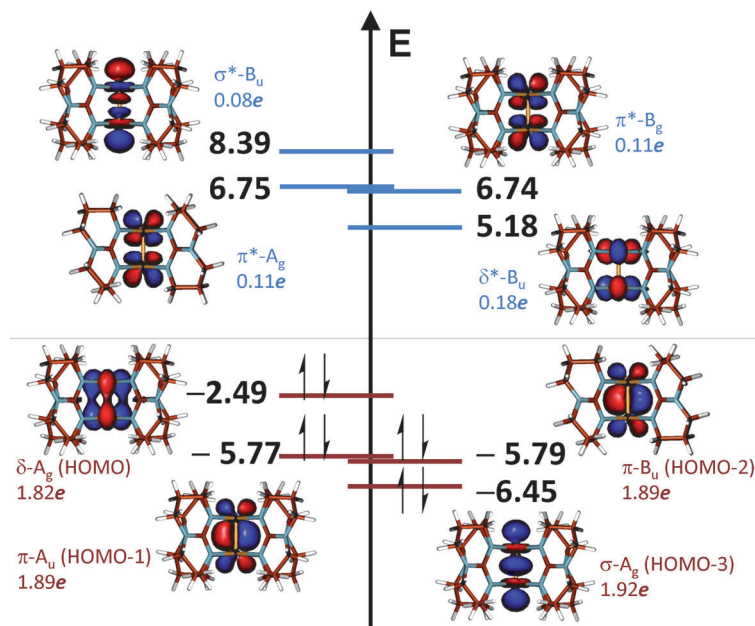


Figure 2. Orbital diagram in terms of energy (in eV) and electron occupancy of $W_2(hpp)_4$ at the level of CASSCF/SARC with DKH2 suggests an EBO of 3.52.

rationalized to the plateau present between 7.0 and 8.0 eV.^[13] Upon excitation by incident UV light, $W_2(hpp)_4$ could possess d–d* transitions to the excited states forming $W_2(hpp)_4^*$, followed by autoionizations to produce the $W_2(hpp)_4^+$ cation.

Although it has been concluded that AE calculations are more precise than ECP calculations,^[24] the pseudopotential approach requires fewer computational resources and is also able to provide accurate results in geometrical and valence properties^[16b,25] that are similar to the AE approach. At the MRCI level the computed IEs of $W_2(hpp)_4$ using ECP and LanL2TZ basis set are consistently lower than the results of AE calculations in each valence ionization, and the deviations are <0.16 eV. For the δ ionization the AE result is closer to the experimental value according to a high-resolution spectral assignment.^[12b] A more balanced approach would be to compare the accuracy of ECP calculations to that of AE calculations for the π and σ photoionization peaks, if their spectral data are available at a superior resolution similar to the scale used in the δ ionization.

The charge redistributions between $M_2(\text{hpp})_4$ and the four cationic states were analyzed at the CASSCF level and are listed in Table S6 (Supporting Information). The deviations in the Mülliken charge prior to and after the IE process show that the ionizations are intrinsic to the metal–metal bonding core, while the changes in Mülliken populations are insignificant at the hpp ligand sites. Multi-configuration calculations also suggest that the di-metal unit of $M_2(\text{hpp})_4$ is computationally closer to an M_2^{3+} core instead of the M_2^{4+} core described by the formal charge: the W_2 core has a slightly less positive charge of +2.97 before ionizations in the neutral $W_2(\text{hpp})_4$, compared with the analogous Mo_2 core of $Mo_2(\text{hpp})_4$, with a charge of +3.21. Visualizations for the charge distributions of $W_2(\text{hpp})_4$ as well as $W_2(\text{hpp})_4^+$ after δ ionization by electrostatic potential (ESP) maps are illustrated in Figure 3.

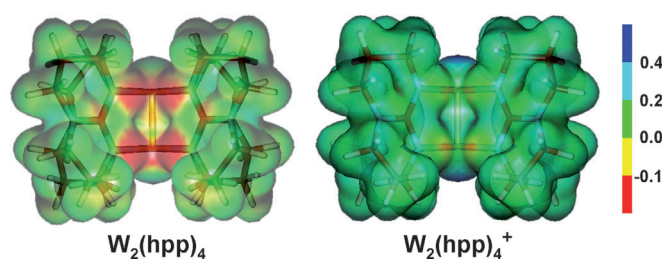


Figure 3. Charge redistribution of the δ ionization in $W_2(\text{hpp})_4$ by ESP maps.

The occupation numbers of the electrons in the occupied and virtual orbitals within the active space of CASSCF wavefunction can be used to calculate the effective bond order (EBO).^[8b] The electron occupancies in the metal–metal bonding as well as antibonding orbitals of $Mo_2(\text{hpp})_4$ and $W_2(\text{hpp})_4$ suggest EBO values of 3.39 and 3.51, respectively, in terms of the ECP LanL2TZ basis set. Relativistic AE calculation using the SARC basis set with both DKH2 and DKH4 corrections give an identical bond order (BO) of 3.52 for $W_2(\text{hpp})_4$. In the natural bond orbital (NBO) theory,^[26] electron occupancy of each orbital is also evaluable (Supporting Information Table S7), and hence a similar scheme can be applied to compute the BO; such EBO calculations based on the BP86 wavefunction with Def2-TZVP and SARC basis sets for $Mo_2(\text{hpp})_4$ and $W_2(\text{hpp})_4$, respectively, yield BO values of 3.29 (Def2-TZVP) and 3.31 (SARC); slightly lower than the BO values given by multi-configuration theory. Both the CASSCF and DFT-NBO analyses conclude a higher BO in the quadruply bonded $W_2(\text{hpp})_4$ complex than its di-molybdenum analogue.

In conclusion, very distinct energetic sequences of δ , π , and σ ionizations corresponding to the quadruple bonds in $Mo_2(\text{hpp})_4$ and $W_2(\text{hpp})_4$ have been revealed by high-level MRCI calculations that incorporate the relativistic effect. The π and σ ionizations in the photoionization spectra of $W_2(\text{hpp})_4$ are explicitly assigned due to the computations. Charge redistribution after the ionization process further

supports that these ionizations are intrinsic to the metal–metal bonding core. Because only few di-molybdenum compounds with quintuple bonds have been experimentally characterized,^[9c] and no W–W quintuply bonded complexes have been reported, it would be intriguing to investigate the IPs of the di-tungsten quintuple bonds after the discovery of such species and to compare the energetics with $M_2(\text{hpp})_4$ reported herein.

Experimental Section

Computational methods: Geometry optimizations were carried out in C_{2h} symmetry using DFT methods with triple- ζ quality basis sets, and the resultant structures were used to calculate the IEs by multi-configuration theories. In addition to the authentic structures of $M_2(\text{hpp})_4$, the simplified model of M_2L_4 ($M=Mo, W$; $L=(NH)_2CNH_2$, see Figure S1 in the Supporting Information) was intentionally constructed and optimized, followed by CASSCF computations to help determine the numbers of active electrons and orbitals. Both of canonical and DFT orbitals suggested to include eight active electrons with eight active orbitals, resulting in the CASSCF(8,8) and CASSCF(7,8) wavefunctions, respectively, in the neutral ground state and doublet ionized states. Internally contracted MRCI calculations based on the converged CASSCF wavefunctions were followed to compute the IEs, and relativistic effect in the tungsten complex was incorporated by the ECP approach as well as by the DKH formalism up to the fourth order in all-electron calculations. Details are available in the Supporting Information.

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Keywords: ionization potentials • metal–metal bonds • multi-reference configuration interactions • quadruple bonds • relativistic effects

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