

Supporting Information

On the Highest Oxidation States of Metal Elements in MO₄ Molecules (M = Fe, Ru, Os, Hs, Sm, and Pu)

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Table S1. Ground State Electronic Configurations of MO₄ Molecules

| Molecule | State | Leading Electronic Configuration ^{a)} | | | | | | | | | |
|---|-----------------------------|--|---|--|------------------------------|------------------------------|------------------------------|--|--|--|--|
| Sm ^{III} (O ₂)(O ₂ [•]) | ⁷ A ₂ | (Core) ⁸² | 1b ₁ ² 1a ₁ ² 1a ₂ ² | 2a₁¹ 1b₂¹ 2b₁¹ 3a₁¹ 2b₂¹ 3b₂¹ | 3a ₂ ⁰ | | | | | | |
| [Pu ^V O ₂](O ₂ [•]) | ⁵ B ₁ | (Core) ¹¹⁴ | 1b ₂ ² 1a ₁ ² 1b ₁ ² 2b ₂ ² | 1a₂¹ 2b₁¹ 2a₁¹ 2a₂¹ | 3b ₂ ⁰ | 3a ₂ ⁰ | | | | | |
| [Fe ^{VI} O ₂](O ₂) | ¹ A ₁ | (Core) ⁴⁶ | 1b ₂ ² 1a ₁ ² 1b ₁ ² 2b ₂ ² 2a ₁ ² | (1a₂&3b₂) ² | 2a ₂ ⁰ | 2b ₁ ⁰ | 3a ₂ ⁰ | | | | |
| Fe ^{VIII} O ₄ | ¹ A ₁ | (Core) ⁴⁶ | 1a ₁ ² 1t ₂ ⁶ 1e ⁴ 2t ₂ ⁶ 2a ₁ ² 3t ₂ ⁶ | (1t₁&2e) ⁶ | 4t ₂ ⁰ | 3a ₁ ⁰ | | | | | |
| Ru ^{VIII} Os ^{VIII} Hs ^{VIII} | O ₄ | ¹ A ₁ (Core) $\left\{ \begin{array}{l} 44 \\ 76 \\ 108 \end{array} \right\}$ | 1a ₁ ² 1t ₂ ⁶ 1e ⁴ 2t ₂ ⁶ 2a ₁ ² 3t ₂ ⁶ 1t ₁ ⁶ | | 2e ⁰ | 4t ₂ ⁰ | 3a ₁ ⁰ | | | | |

^{a)} Singly or fractionally occupied MOs are in **bold** face, empty MOs are in *italic*.

Table S2. Total energies E_q of atomic cations M^{q+} (in eV).^{a)}

| q ^{b)} | Config. ^{c)} | Fe | Ru | Os | Hs | Config. ^{c)} | Sm | Config. ^{c)} | Pu |
|-------------------------------------|------------------------------|----------------|---------------|--------------------|--------------------|--|---------------|--------------------------------|---------------|
| 0 | d ⁸ | -0- | -0- | -0- ^{d)} | -0- ^{e)} | f ⁶ d ¹ s ¹ | -0- | f ⁶ s ² | -0- |
| 1 | d ⁷ | 4.0 | 7.3 | 8.4 ^{d)} | 7.6 ^{e)} | f ⁶ d ¹ | 5.2 | f ⁶ s ¹ | 6.0 |
| 2 | d ⁶ | 20.0 | 24.0 | 25.4 ^{d)} | 25.8 ^{e)} | f ⁶ | 15.4 | f ⁶ | 18. |
| 3 | d ⁵ | 50.7 | 52.5 | 50.4 | 55.1 ^{e)} | f ⁵ | 38.9 | f ⁵ | 39. |
| 4 | d ⁴ | 105.6 | 98. | 91. | 93. | f ⁴ | 80.3 | f ⁴ | 74. |
| 5 | d ³ | 180.6 | 157. | 146. | 144. | f ³ | 143. | f ³ | 123. |
| 6 | d ² | 279.5 | 233. | 217. | 208. | f ⁴ p ⁻² | 231. (235) | f ³ p ⁻¹ | 203. (191) |
| 7 | d ¹ | 404.5 | 326. | 302. | 286. | f ⁴ p ⁻³ | 331. (360) | f ² p ⁻² | 298. (281) |
| 8 | d ⁰ | 555.6 | 436. | 404. | 378. | f ⁴ p ⁻⁴ | 451. (523) | f ³ p ⁻³ | 408. (396) |
| 9 | p ⁻¹ | 789.2 (740) | 614. (567) | 572. (527) | 538. (485) | f ⁴ p ⁻⁵ | 592. (729) | f ³ p ⁻⁴ | 528. (539) |
| 10 | p ⁻² | 1051. (956) | 812. (719) | 762. (670) | 712. (609) | f ⁴ p ⁻⁶ | 750. (985) | f ² p ⁻² | 667. (712) |
| <i>a</i> | | -4.490 | 0.546 | 2.634 | 3.824 | | 3.758 | | 3.667 |
| <i>b</i> | | 6.236 | 5.229 | 4.220 | 4.305 | | 0.575 | | 1.627 |
| <i>c</i> | | 0.377 | 0.190 | 0.222 | 0.140 | | 0.890 | | 0.513 |
| Δ | | 1.2 | 0.8 | 1.2 | 0.5 | | 0.3 | | 0.3 |

^{a)} The energy of M^0 is chosen as zero. The ionic energies are from the NIST Atomic Spectra Database (Kramida A, Ralchenko Y, Reader J, & NIST ASD Team (2012), available at <http://physics.nist.gov/asd>). The bold energy entries indicate the highest stable oxidation state of M in M·O species. Where available, we choose the ground states of the (d or f)^{8-q} configurations of the free atoms, i.e. the systematic series typically appearing as ‘atoms in ground state molecules’.

^{b)} q = atomic charge; a , b , c are the parameters in the energy fit $E_q \approx a \cdot q + b \cdot q^2 + c \cdot q^3$; for Fe, Ru, Os, Hs, the cubic is fitted to $q = 0$ through 8, but for Sm and Pu to $q = 0$ through 5; Δ is the standard deviation of the fit (in eV). The energy values in parentheses are the extrapolated values of the fit to the valence shell ionization energies for the higher p⁶ core shell ionizations, which deviate greatly.

^{c)} Config. = electron configuration from which the chosen state derives, with reference to the chemically common naked atomic cores; p⁻ⁿ indicates n missing electrons in the outer p⁶ core shell;

^{d)} For Os⁰, Os¹⁺, Os²⁺, the available lowest state configurations were d⁶s², d⁷s¹, d⁵s¹, respectively.

^{e)} For Hs⁰, Hs¹⁺, Hs²⁺, Hs³⁺, the available lowest state configurations were d⁶s², d⁵s², d⁵s¹, d⁴s¹, respectively.