Calculated Ionization Potentials of MO_3 and MO_2 for M = U, Mo, W and Nd

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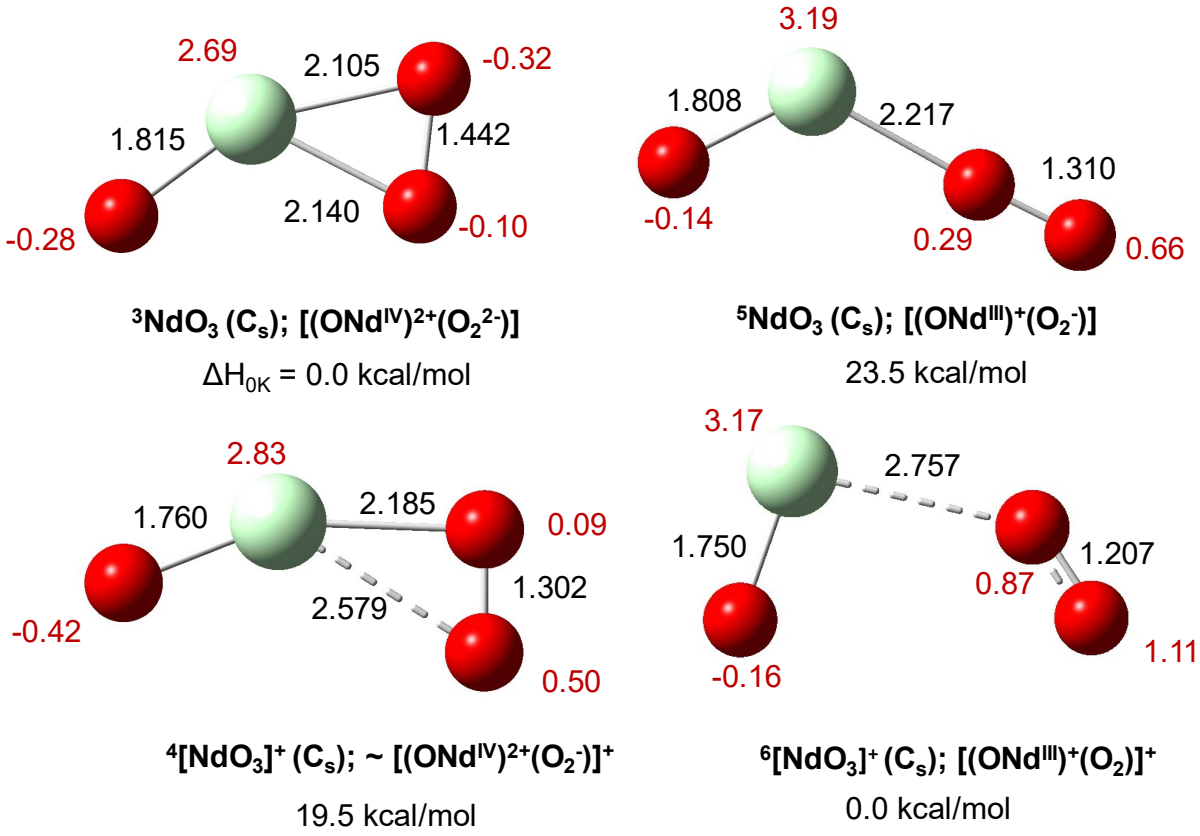

$^{3}NdO_3$ (C_s); [(ONd^{IV})$^{2+}$(O_2^{2-})]

ΔH_{0K} = 0.0 kcal/mol

$^{5}NdO_3$ (C_s); [(ONd^{III})$^{+}$(O_2^{-})]

23.5 kcal/mol

$^{4}[NdO_3]^{+}$ (C_s); ~ [(ONd^{IV})$^{2+}$(O_2^{-})]$^{+}$

19.5 kcal/mol

$^{6}[NdO_3]^{+}$ (C_s); [(ONd^{III})$^{+}$(O_2)]$^{+}$

0.0 kcal/mol

Figure S1. Mulliken spins, relative energies and geometry parameters at B3LYP//aD/Stutt-ECP

Table S1. Contributions to the final FPD composite result for the IP_0 of UO_3 and UO_2 in eV using aug-cc-pV*n*Z(-PP) basis sets *n* = D, T, and Q.

Calculation	**UO_3**	**$^3UO_2$**
ΔE(aD/D-PP)	9.25	6.03
ΔE(aT/T-PP)	9.46	6.06
ΔE(aQ/Q-PP)	9.53	6.07
ΔE(CBS)	9.58	6.07
ΔCV	0.002	0.02
ΔSO	0.048	0.034
ΔGaunt	-0.015	-0.030
ΔLamb	0.001	-0.02
ΔZPE	0.002	0.009
IP_0 (FPD)	9.62	6.08

Table S2. Contributions to the final FPD composite result for the IP_0 of MO_3 and MO_2 in eV for M = W and Mo using aug-cc-pV*n*Z(-PP) basis sets *n* = D, T, and Q.

Calculation	**WO_3**	**MoO_3**	**$^1WO_2$**	**$^3MoO_2$**
ΔE(aD/D-PP)	10.86	10.86	8.61	8.38
ΔE(aT/T-PP)	11.00	11.00	8.66	8.38
ΔE(aQ/Q-PP)	11.07	11.17	8.68	8.40
ΔE(CBS)	11.11	11.12	8.69	8.41
ΔCV	0.05	0.05	0.06	0.10
ΔSO	0.020	0.002	0.034	-0.002
ΔGaunt	-0.009	-0.006	-0.010	-0.001
ΔSR	-0.02	-0.01	0.01	-0.01
ΔZPE	-0.04	-0.03	0.004	0.01
IP_0 (FPD)	11.11	11.13	8.79	8.51

Table S3. Contributions to the final FPD composite result for the IP_0 of $^3NdO_2$ in eV using aug-cc-pV*n*Z-DK for O and cc-pV*n*Z-DK3 for Nd basis sets.

Calculation	**$^3NdO_2$**
ΔE(aD-DK/D-DK3)	8.08
ΔE(aT-DK/T-DK3)	8.07
ΔE(aQ-DK/Q-DK3)	8.11
ΔE(CBS)	8.13
ΔSO	-0.26
ΔGaunt	-0.00
ΔZPE	0.04
IP_0 (FPD)	7.91

Table S4. NPA charges (q) from NBO7 implemented in Molpro.2018 (HF orbitals) using aug-cc-pVDZ-DK(O)/cc-pVDZ-DK3(U, Nd) basis sets for U and Nd oxides and aug-cc-pVDZ(O)/aug-cc-pVDZ-PP (Mo, W) basis sets for Mo and W oxides.

Molec	Sym	q(U)	q(O)	q(O)
$^{1}UO_3$	C_{2v}	2.626	-0.942	-0.842 (x2)
$^{2}UO_3^{+}$	C_{2v}	2.820	-0.449	-0.685 (x2)
$^{3}UO_2$	$D_{\infty h}$	1.970	-0.985 (x2)	
$^{2}UO_2^{+}$	$D_{\infty h}$	2.763	-0.882 (x2)	
$^{1}WO_3$	C_{3v}	2.561	-0.854 (x3)	
$^{2}WO_3^{+}$	C_s	2.586	-0.345	-0.610 (x2)
$^{1}WO_2$	C_{2v}	1.601	-0.801 (x2)	
$^{2}WO_2^{+}$	C_{2v}	2.268	-0.634 (x2)	
$^{1}MoO_3$	C_{3v}	2.411	-0.803 (x3)	
$^{2}MoO_3^{+}$	C_s	2.429	-0.371	-0.529(x2)
$^{3}MoO_2$	C_{2v}	1.877	-0.938 (x2)	
$^{2}MoO_2^{+}$	C_{2v}	2.214	-0.607 (x2)	
$^{3}NdO_2$	$D_{\infty h}$	2.678	-1.134 (x2)	
$^{2}NdO_2^{+}$	$D_{\infty h}$	2.520	-0.760 (x2)	

Table S5. NBOs and Spins (Natural Spin Densities) for metal atoms **(**U, W, Mo and Nd).

Molec	U spin	5f total	5fα	5fβ	5f(α-β)	6p total	6pα	6pβ	6p(α-β)	6d total	6dα	6dβ	6d(α-β)	7s total	7sα	7s β	7s(α-β)
$^{1}UO_3$	0	2.03				5.69				1.55				0.01			
$^{2}UO_3^{+}$	0.03	2.07	1.05	1.03	0.02	5.64	2.82	2.82	0.00	1.37	0.69	0.68	0.01	0.05	0.02	0.02	0.00
$^{3}UO_2$	1.95	2.39	1.69	0.70	0.99	5.76	2.88	2.88	0.00	0.93	0.53	0.40	0.13	0.87	0.84	0.03	0.81
$^{2}UO_2^{+}$	1.00	2.58	1.78	0.80	0.98	5.72	2.86	2.86	0.00	0.86	0.43	0.43	0.00	0.03	0.02	0.02	0.00

Molec	W spin	5d total	5dα	5dβ	5d(α-β)	6s total	6sα	6sβ	6p total
$^{1}WO_3$	0.0	3.20				0.17			
$^{2}WO_3^{+}$	0.01	3.17	1.59	1.58	0.01	0.19	0.09	0.09	
$^{1}WO_2$	0.0	3.07				1.22			0.07
$^{2}WO_2^{+}$	0.96	3.27	1.96	1.31	0.65	0.42	0.36	0.06	

Molec	Mo spin	4d total	4dα	4dβ	4d(α-β)	4p total	4pα	4pβ	4p(α-β)	5s total	5sα	5sβ	5s(α-β)
$^{1}MoO_3$	0.0	3.49				5.94				0.10			
$^{2}MoO_3^{+}$	0.01	3.46	1.74	1.73	0.01	5.93	2.97	2.97	0.00	0.12	0.06	0.06	0.00
$^{3}MoO_2$	1.84	3.81	2.69	1.12	1.57	5.95	2.98	2.97	0.01	0.28	0.24	0.03	0.21
$^{2}MoO_2^{+}$	0.87	3.67	2.23	1.45	0.78	5.94	2.97	2.97	0.00	0.14	0.11	0.03	0.08

Molec	Nd spin	4f total	4fα	4fβ	4f(α-β)	5p total	5pα	5pβ	5p(α-β)	5d total	5dα	5dβ	5d(α-β)	6s total	6sα	6s β	6s(α-β)
$^{3}NdO_2$	2.00	3.01	2.49	0.51	1.98	5.78	2.89	2.89	0.00	0.84	0.42	0.42	0.00	0.04	0.02	0.02	0.00
$^{2}NdO_2^{+}$	1.00	2.91	1.95	0.96	0.99	5.54	2.77	2.77	0.00	0.95	0.48	0.48	0.00	0.04	0.02	0.02	0.00

Table S6. NBOs and spins (Natural spin densities) for the oxygen atoms

Molec	O spin	O spin	O spin	O2p	α	β	2p(α-β)	O2p	α	β
$^{1}UO_3$	0.0			5.03				4.94(x2)		
$^{2}UO_3^+$	0.95	0.01(x2)		4.51	2.73	1.78	0.95	4.79(x2)	2.40	2.39
$^{3}UO_2$	0.02			5.07	2.54	2.52	0.02			
$^{2}UO_2^+$	0.00			4.95	2.48	2.48	0.00			
$^{1}WO_3$	0.0			4.93						
$^{2}WO_3^+$	0.95	0.02(x2)		4.41	2.68	1.73	0.95	4.68(x2)	2.35	2.33
$^{1}WO_2$	0.0			4.89						
$^{2}WO_2^+$	0.02			4.70	2.36	2.34	0.02			
$^{1}MoO_3$	0.0			4.87						
$^{2}MoO_3^+$	0.96	0.02 (x2)		4.41	2.68	1.73	0.95	4.59	2.30	2.29
$^{3}MoO_2$	0.08			4.99	2.53	2.46	0.07			
$^{2}MoO_2^+$	0.06			4.66	2.36	2.30	0.06			
$^{3}NdO_2$	0.002			5.18	2.59	2.59	0.00			
$^{2}NdO_2^+$	0.00			4.83	2.41	2.41	0.00			

Table S7. IPs for NdO_3

IP (eV)	N=D	N=T
$^{3}NdO_3$ / $^{4}[NdO_3]^+$		
B3LYP//aD/Stutt-ECP	8.93	
aN-DK/N-DK3 (HF)	8.84	8.99
aN-DK/N-DK3 (PW91)	8.87	9.02
$^{3}NdO_3$ / $^{6}[NdO_3]^+$		
B3LYP//aD/Stutt-ECP	8.09	
aN-DK/N-DK3 (PW91)	7.80	

Table S8. CASSCF analysis.

$^{3}NdO_3$

CI vector for state symmetry 1

aa00 000	0.7175767
0000 aa0	-0.6962497
TOTAL ENERGIES	-9845.01657717

CI vector for state symmetry 2

a000 a00	0.7628426
0a00 0a0	0.6463034
TOTAL ENERGIES	-9845.01671752

$^{5}NdO_3$

CI vector for state symmetry 1

aa000000 aa000	0.6766513
aaaa0000 00000	-0.6149687
a0a00000 a0a00	0.3088305
a00a0000 0aa00	0.2514537
TOTAL ENERGIES	-9845.13306276

CI vector for state symmetry 2

aaa00000 a0000	0.6890486
aa0a0000 0a000	0.6028482
a0000000 aaa00	-0.2995280
a0aa0000 00a00	0.2566127
TOTAL ENERGIES	-9845.13308327

$^{4}NdO_3^{+}$

CI vector for state symmetry 1

aaa00000 00000	0.7075562
a0000000 aa000	0.7058009
TOTAL ENERGIES	-9844.74407230

CI vector for state symmetry 2

aa000000 a0000	0.7143562
a0a00000 0a000	-0.6989164
TOTAL ENERGIES	-9844.74408187

$^{6}NdO_3^{+}$

CI vector for state symmetry 1

aaa00000 aa000	0.8448597
aa0a0000 a0a00	0.3620397
a0aa0000 a00a0	0.3332533
a0000000 aaaa0	-0.1541109
a00aa000 aa000	-0.0933728
aa00a000 a00a0	0.0676824
a0a0a000 a0a00	-0.0520835
TOTAL ENERGIES	-9844.90490301

CI vector for state symmetry 2

aaaa0000 a0000	0.7580515
aa000000 aaa00	-0.4964032
a0a00000 aa0a0	-0.3827338
a00a0000 a0aa0	-0.1645365
TOTAL ENERGIES	-9844.90433989

Table S9. Total Energies at the CCSD(T) Level of Theory in Atomic Units.

Molecule	aD/(a)D-PP	aD/(a)D-PP	aD/(a)D-PP	CBS	awD-DK/ wD-DK3	awT-DK/ wT-DK3	awQ-DK/ wQ-DK3	CBS
$^{1}UO_3$	-698.4593267	-698.7235857	-698.8119195	-698.8624859	-28226.057660	-28226.651150	-28226.839476	-28226.946233
$^{2}UO_3^{+}$	-698.799410	-699.071199	-699.1622301	-699.2143593	-28225.717552	-28226.304051	-28226.489878	-28226.595187
$^{3}UO_2$	-623.658694	-623.864769	-623.935093	-623.975500	-28150.821043	-28151.335150	-28151.501276	-28151.595776
$^{2}UO_2^{+}$	-623.437050	-623.642079	-623.712083	-623.752309	-28150.596142	-28151.110420	-28151.276971	-28151.371754
					awD/awD-PP	awT/awT-PP	awQ/awQ-PP	CBS
$^{1}WO_3$	-292.260902	-292.479364	-292.545736	-292.583037	-292.638406	-292.977852	-293.074433	-293.127959
$^{2}WO_3^{+}$	-291.8617405	-292.0751632	-292.1390269	-292.174806	-292.237897	-292.571731	-292.665728	-292.717702
$^{1}WO_2$	-217.122875	-217.277001	-217.323125	-217.348967	-217.464771	-217.719995	-217.792481	-217.832638
$^{2}WO_2^{+}$	-216.806607	-216.958760	-217.004143	-217.029551	-217.145624	-217.399198	-217.471277	-217.511215
$^{1}MoO_3$	-292.7975617	-293.013811	-293.081438	-293.119666	-293.220914	-293.562335	-293.659758	-293.713786
$^{2}MoO_3^{+}$	-292.398462	-292.609645	-292.674580	-292.711163	-292.820817	-293.156394	-293.251093	-293.303480
$^{3}MoO_2$	-217.663773	-217.814623	-217.861830	-217.888518	-218.050130	-218.307182	-218.381366	-218.422607
$^{2}MoO_2^{+}$	-217.355712	-217.506521	-217.553145	-217.579440	-217.740554	-217.996140	-218.069339	-218.109966
	aD/D-DK3	aD/D-DK3	aD/D-DK3	CBS	awD-DK/ wD-DK3	awT-DK/ wT-DK3	awQ-DK/ wQ-DK3	CBS
$^{3}NdO_2$	-9771.083553	-9771.304116	-9771.370696	-9771.408065	-9771.785565	-9772.351578	-9772.530652	-9772.632105
$^{2}NdO_2^{+}$	-9770.786734	-9771.007476	-9771.072806	-9771.109322	-9771.497196	-9772.057804	-9772.234054	-9772.333786

Table S10. XYZ coordinates optimized at B3LYP/aug-cc-pVDZ(O)/cc-pVDZ-PP(U)/aug-cc-pVDZ-PP(Mo,W)/Stuttgart-ECP(Nd)

UO_3 (C_{2v})
0 1

U	0.000000	0.000000	0.078944
O	0.000000	0.000000	-1.777942
O	0.000000	1.777504	0.435043
O	0.000000	-1.777504	0.435043

UO_3^+ (C_{2v})
1 2

U	0.000000	0.000000	0.127967
O	0.000000	0.000000	-1.873850
O	0.000000	1.746804	0.201114
O	0.000000	-1.746804	0.201114

UO_2 ($D_{\infty h}$)
0 3

U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.802208
O	0.000000	0.000000	-1.802208

UO_2^+ ($D_{\infty h}$)
1 2

U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.766097
O	0.000000	0.000000	-1.766097

WO_3 (C_{3v})
0 1

W	0.000000	0.000000	0.150940
O	0.000000	1.611834	-0.465399
O	1.395890	-0.805917	-0.465399
O	-1.395890	-0.805917	-0.465399

WO_3^+ (C_s)
1 2

W	0.180563	0.021608	0.000000
O	-0.556737	-1.650213	0.000000
O	-0.556737	0.725169	1.352564
O	-0.556737	0.725169	-1.352564

WO_2 (C_{2v})
0 1

W	0.000000	0.000000	0.182843
O	0.000000	1.335603	-0.845647

O 0.000000 -1.335603 -0.845647

WO_2^+ (C_{2v})
1 2
W 0.000000 0.000000 0.184260
O 0.000000 1.311030 -0.852203
O 0.000000 -1.311030 -0.852203

MoO_3 (C_{3v})
0 1
O 0.000000 1.629215 -0.337531
O 1.410942 -0.814608 -0.337531
O -1.410942 -0.814608 -0.337531
MO 0.000000 0.000000 0.192875

MoO_3^+ (C_s)
1 2
O -0.429097 -1.687472 0.000000
O -0.429097 0.760763 1.347167
O -0.429097 0.760763 -1.347167
MO 0.245199 0.031609 0.000000

MoO_2 (C_{2v})
0 3
O 0.000000 1.442104 -0.659962
O 0.000000 -1.442104 -0.659962
MO 0.000000 0.000000 0.251414

MoO_2^+ (C_{2v})
1 2
O 0.000000 1.332705 -0.723350
O 0.000000 -1.332705 -0.723350
MO 0.000000 0.000000 0.275562

NdO_3 (C_s)
0 3
O -1.494281 -1.198882 0.000000
O -0.205965 -1.846890 0.000000
O 1.700246 0.919616 0.000000
ND 0.000000 0.283487 0.000000

NdO_3 (C_s)
0 5
O -0.644605 -1.650510 0.000000
O -1.082168 -2.885101 0.000000
O 1.726772 1.006578 0.000000

ND 0.000000 0.470538 0.000000

NdO_3^+ (C_s)
1 4
O -1.273592 -1.447612 0.000000
O -0.239752 -2.239477 0.000000
O 1.513344 1.225833 0.000000
ND 0.000000 0.328167 0.000000

NdO_3^+ (C_s)
1 6
O -1.057949 -1.907462 0.000000
O -0.622259 -3.032958 0.000000
O 1.680208 0.147792 0.000000
ND 0.000000 0.639017 0.000000

NdO_2 ($D_{\infty h}$)
0 3
O 0.000000 0.000000 1.814867
O 0.000000 0.000000 -1.814867
ND 0.000000 0.000000 0.000000

NdO_2^+ ($D_{\infty h}$)
1 2
O 0.000000 0.000000 1.690373
O 0.000000 0.000000 -1.690373
ND 0.000000 0.000000 0.000000