

Supplementary information: Soft x-ray signatures of ionic manganese-oxo systems, including a high-spin manganese(V) complex

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1 Computational settings

Table 1: Additional details about the RAS simulations by molecule and valence state, including the number of core excited states, energy shifts and relative intensity scaling (RIS) for theoretical spectra to match experiment, and the similarity between theoretical and experimental spectra from the weighted cross-correlation function.

Molecule and state	K-edge				L-edge			
	Nr of states	Shift (eV)	RIS	Similarity	Nr of states	Shift (eV)	RIS	Similarity
MnO ⁺ ⁵ Π	60x4 = 240	-0.860	1	0.992	130x4x2+40x4 = 1200	-1.908	1	0.999
MnO ⁺ ⁵ Σ	60x4 = 240	-0.980	1.09	0.881	100x4x2+3x3 = 809	-1.770	1.03	0.993
MnO ₂ ⁺ ³ B ₁	60x4 = 240	-0.384	1	0.998	120x4x3 = 1440	-1.606	1	0.996
MnO ₂ ⁺ ¹ B ₁	60x4 = 240	-0.816	0.96	0.995	120x4x2 = 960	-1.794	1.08	0.990
MnO ₃ ⁺ ¹ A ₁	60x2 = 120	-1.480	1	0.991				

2 Additional information on theoretical geometric and electronic structures

Table 2: Mulliken charge populations for all complexes and electronic states.

Molecule	Geometry	State	Charges		
			Mn	O (oxo)	O ₂
MnO ⁺	Linear C _∞	⁵ Π	1.42	-0.42	
		⁵ Σ ⁺	1.55	-0.55	
		⁷ Π	1.49	-0.49	
MnO ₂ ⁺	Bent C _{2v}	³ B ₁	1.58	-0.29	
		¹ B ₁	1.53	-0.26	
MnO ₃ ⁺	Pyramidal C _{3v} side-on superoxo C _s	¹ A ₁	1.54	-0.18	
		³ A'	1.47	-0.56	0.09
	Pyramidal C _{3v} end-on O ₂ C _s	³ A ₂	1.52	-0.17	
		¹ A ₂	1.52	-0.17	
MnO ₄ ⁺	side-on superoxo C _{2v}	³ A''	1.49	-0.47	-0.02
		¹ A ₂	1.51	-0.29	0.06
	peroxo-superoxo C _{2v}	³ A ₂	1.51	-0.29	0.06
		³ A ₁	1.44		0.07/-0.50
end-on O ₂ C _s	¹ A''	1.55	-0.34	0.12	
	³ A''	1.57	-0.35	0.13	
MnO	Linear C _∞	⁶ Σ ⁺	0.77	-0.77	
MnO ²⁺	Linear C _∞	⁴ Σ ⁻	1.81	0.19	
MnO ₂	Bent C _{2v}	⁴ B ₂	1.36	-0.68	

Table 3: Geometric parameters for all complexes and electronic states.

Molecule	Structure	Mn-O (Å)	O-Mn-O (°)	Mn-OO (Å)	O-O(Å)	Mn-O-O(°)
MnO ⁺	⁵ Π	1.675				
	⁵ Σ	1.593				
	⁷ Π	1.841				
MnO ₂ ⁺	³ B ₁	1.584	119.6			
	¹ B ₁	1.570	117.6			
MnO ₃ ⁺	¹ A ₁	1.610	118.8			
	³ A'	1.615	146.0	1.899	1.306	69.9
	³ A ₂	1.618	113.0			
	¹ A ₂	1.623	116.1			
	³ A''	1.721	160.8	2.055	1.218	155.8
MnO ₄ ⁺	¹ A ₂	1.523	119.3	1.864	1.255	70.3
	³ A ₂	1.523	119.3	1.866	1.254	70.4
	³ A ₁			1.900/1.770	1.258/1.388	70.7/66.9
	¹ A''	1.544	119.9	1.969	1.200	151.9
	³ A''	1.544	119.9	1.969	1.200	151.9
MnO	⁶ Σ ⁺	1.622				
MnO ₂ ²⁺	⁴ Σ ⁻	2.120				
MnO ₂	⁴ B ₂	1.639	118.4			

3 Convergence of spectra with theoretical parameters

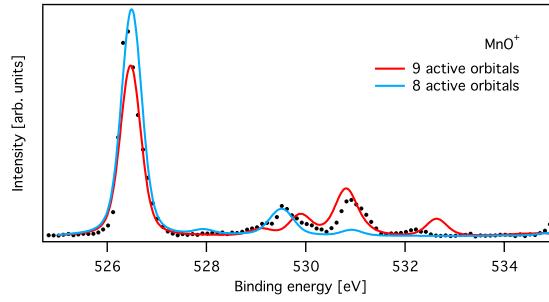


Figure S1: Theoretical oxygen K-edge XAS spectra of [MnO]⁺ with 8 or 9 active orbitals.

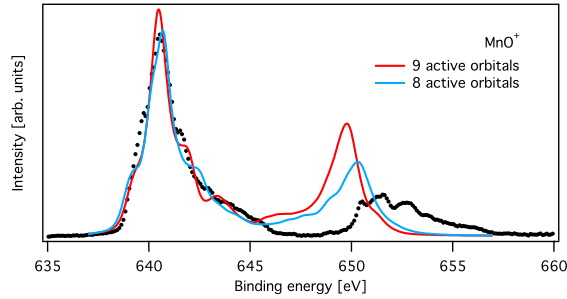


Figure S2: Theoretical manganese L-edge XAS spectra of [MnO]⁺ with 8 or 9 active orbitals.

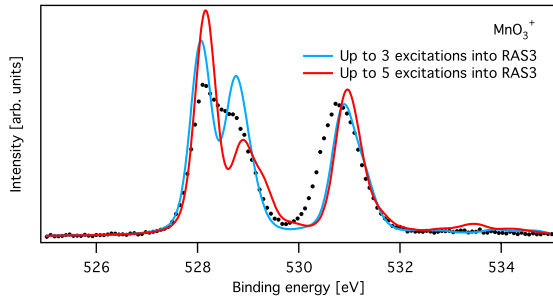


Figure S3: Theoretical oxygen K-edge XAS spectra of $[\text{MnO}_3]^+$ with 3 or 5 excitations into the RAS3 space. The alignment difference between 3 and 5 excitations is 0.32 eV.

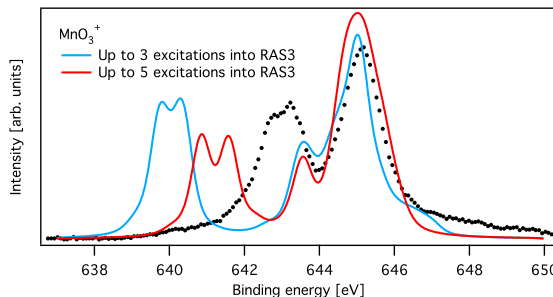


Figure S4: Theoretical manganese L-edge XAS spectra of $[\text{MnO}_3]^+$ with 3 or 5 excitations into the RAS3 space. The alignment difference between 3 and 5 excitations is 2.92 eV.

4 Comparison of oxygen K-edge positions

The O K-edge absorption onsets, plotted versus the number of oxygen atoms, are given in Figure S5. The first observation is that the relative onset positions strongly depend on the measure used to assign it. Second, there is no clear correlation between onset position and the formal oxidation state of oxygen. Considering the partial electron transfer from oxygen to Mn in MnO^+ , and the presence of O_2 -species in $[\text{MnO}_4]^+$, the average oxidation states of these two should be higher than for the other complexes. Still, their onset positions are at opposite ends of the comparison. Another potential correlation would be with the manganese oxidation state because the probed unoccupied orbitals are formally metal levels. This is only true because most oxygens are oxo, which do not have any formally empty valence levels. Yet, while this hypothesis could possibly justify the shift between MnO^+ and MnO_2^+ , it cannot explain the shifts or lack thereof between the other three complexes.

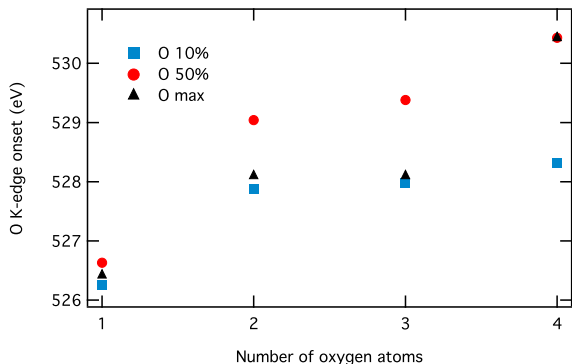


Figure S5: Experimental O K-edge absorption onsets plotted versus the number of oxygen atoms in $[\text{MnO}_n]^+$ ($n=1-4$). The onset positions have been calculated according to three different measures: 10% (resp 50%) refer to the energy at which the accumulated intensity reaches 10% (resp 50%) of the integrated intensity up to 534 eV, while max refers to the energy of the edge maximum.

5 Theoretical MnO-MnO²⁺ series

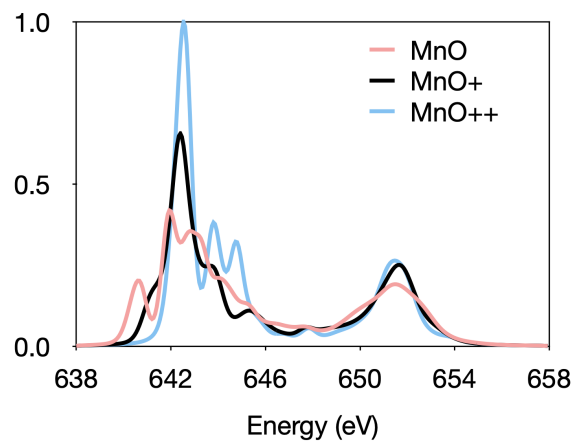


Figure S6: Calculated L-edge XAS spectra of MnO to MnO²⁺ at their relaxed geometries. The relative shift of MnO⁺ and MnO²⁺ compared to MnO are respectively 0.4 eV and 0.53 eV using the maximum edge position and -0.26 eV and -0.2 eV using the median.