Supporting Information

Photoelectron Spectroscopy of Doubly and Singly Charged Group VIB Dimetalate

Anions: $\text{M}_2\text{O}_7^{2-}$, $\text{MM}'\text{O}_7^{2-}$, and M_2O_7^- (M, M' = Cr, Mo, W)

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Table S1. Vertical detachment energies of $\text{M}_2\text{O}_7^{2-}$ (M = Cr, Mo, W) calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectra.

Table S2. Vertical detachment energies of CrMoO_7^{2-} calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectrum. Experimental VDEs for CrWO_7^{2-} and MoWO_7^{2-} are also included.

Table S3. Vertical detachment energies of W_2O_7^- calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectrum.

Figure S1. Photoelectron spectra for $\text{Cr}_2\text{O}_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

Figure S2. Photoelectron spectra for $\text{Mo}_2\text{O}_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

Figure S3. Photoelectron spectra for $\text{W}_2\text{O}_7^{2-}$ at (a) 193 nm and (b) 157 nm.

Figure S4. Photoelectron spectra for CrMoO_7^{2-} at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

Figure S5. Photoelectron spectra for CrWO_7^{2-} at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

Figure S6. Photoelectron spectra for MoWO_7^{2-} at (a) 193 nm and (b) 157 nm.

Table S1. VDEs of $M_2O_7^{2-}$ (M = Cr, Mo, W) calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectra.

species	theor VDE ^a		assignment ^b	
	MO	VDE (eV)	feature	expt VDE (eV)
$Cr_2O_7^{2-}$	a_{2g}	1.42	X	~1.30
	a_{1u}	1.42		
	e_u	1.50		
	e_g	2.17	A	2.04 (5)
	a_{2u}	2.84	B	2.65 (5)
	e_u	2.87		
	a_{1g}	2.96		
	a_{2u}	3.85	C	3.40 (5)
	e_g	4.22		
$Mo_2O_7^{2-}$	a_{2g}	1.93	X	~2.2
	a_{1u}	1.93		
	e_u	2.12	A	~2.5
	e_g	2.24		
	a_{2u}	2.65	B	3.05 (5)
	a_{1g}	2.80		
	e_u	2.90		
	a_{2u}	3.82	C	3.82 (5)
	a_{1g}	4.34	D	4.47 (5)
$W_2O_7^{2-}$	e_g	4.35		
	$(1a_{2g})^2$	1.97	X	~2.3
	$(1a_{1u})^2$	1.98		
	$(7e_u)^4$	2.21	A	~2.6
	$(6e_g)^4$	2.29		
	$(7a_{2u})^2$	2.79	B	3.0-3.6
	$(8a_{1g})^2$	3.05		
	$(6e_u)^4$	3.09		
	$(6a_{2u})^2$	4.20	C	4.3-4.7
	$(5e_g)^4$	4.26		
	$(7a_{1g})^2$	4.43		

^aThe ground state electronic configuration for the $W_2O_7^{2-}$ (D_{3d} , $^1A_{1g}$) dianion (**1** in Figure 4) is:

$(7a_{1g})^2(5e_g)^4(6a_{2u})^2(8a_{1g})^2(7a_{2u})^2(6e_g)^4(7e_u)^4(1a_{1u})^2(1a_{1u})^2(1a_{2g})^2$. Similar electronic configurations are found for $Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$ with D_{3d} symmetry.

^bNumbers in parentheses represent the experimental uncertainties in the last digit.

Table S2. VDEs of CrMoO_7^{2-} calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectrum. Experimental VDEs for CrWO_7^{2-} and MoWO_7^{2-} are also included.

species	theor VDE ^a		assignment ^b	
	MO	VDE (eV)	feature	exp VDE (eV)
CrMoO_7^{2-}	a_2	1.68	X	1.85 (5)
	a_2	1.73		
	e	1.86		
	e	2.15	A	2.24 (5)
	a_1	2.49	B	2.55 (5)
	e	2.96	C	2.96 (3)
	a_1	3.19		
	a_1	3.74	D	3.61 (3)
	e	4.32	E	4.15 (5)
	a_1	4.48		
CrWO_7^{2-}			X	1.94 (4)
			A	2.39 (5)
			B	2.81 (5)
			C	3.15 (5)
			D	3.94 (3)
MoWO_7^{2-}			X	2.40 (5)
			A	2.65 (5)
			B	~3.0
			C	3.15 (5)
			D	4.17 (5)
			E	~4.6

^aThe ground state electronic configuration for the mixed dianion CrMoO_7^{2-} with C_{3v} linear geometry is $(a_1)^2(e)^4(a_1)^2(a_1)^2(e)^4(a_1)^2(e)^4(a_2)^2(a_2)^2$.

^bNumbers in parentheses represent the experimental uncertainties in the last digit.

Table S3. VDEs of W_2O_7^- calculated using the generalized Koopman's theorem and tentative assignment of the experimental photoelectron spectrum.

	theor VDE ^a				assignment ^b	
	MO	VDE (eV)	MO	VDE (eV)	feature	exp VDE (eV)
W_2O_7^-			43a (α)	6.61	X	~6.7
	42a (β)	6.61				
	41a (β)	6.77				
	40a (β)	6.93	42a (α)	6.94	A	~7.2
	39a (β)	7.03	41a (α)	7.02		
	38a (β)	7.17	40a (α)	7.10		
	37a (β)	7.31	39a (α)	7.26		
			38a (α)	7.40		
	36a (β)	7.58	37a (α)	7.73	B	7.62 (5)
	35a (β)	7.66				
	34a (β)	7.90	36a (α)	7.82		

^aThe ground state electronic configuration for the W_2O_7^- (C_I , 2A) anion (**2a** in Figure 4) is:

$(37a)^2(38a)^2(39a)^2(40a)^2(41a)^2(42a)^2(43a)^1$.

^bNumbers in parentheses represent the experimental uncertainties in the last digit.

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Figure S2. Photoelectron spectra for $\text{Mo}_2\text{O}_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

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