Supporting Information

Photoelectron Spectroscopy of Doubly and Singly Charged Group VIB Dimetalate Anions: $M_2O_7^{2-}$, $MM'O_7^{2-}$, and $M_2O_7^-$ (M, M' = Cr, Mo, W)

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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} a_{1u} e_u	1.42 1.42 1.50	X	~1.30
	e_g	2.17	A	2.04 (5)
	a_{2u} e_u a_{1g}	2.84 2.87 2.96	B	2.65 (5)
	a_{2u}	3.85	C	3.40 (5)
	e_g a_{1g}	4.22 4.29		
$Mo_2O_7^{2-}$	a_{2g} a_{1u}	1.93 1.93	X	~2.2
	e_u e_g	2.12 2.24	A	~2.5
	a_{2u} a_{1g} e_u	2.65 2.80 2.90	B	3.05 (5)
	a_{2u}	3.82	C	3.82 (5)
	a_{1g} e_g	4.34 4.35	D	4.47 (5)
$W_2O_7^{2-}$	$(1a_{2g})^2$ $(1a_{1u})^2$	1.97 1.98	X	~2.3
	$(7e_u)^4$ $(6e_g)^4$	2.21 2.29	A	~2.6
	$(7a_{2u})^2$ $(8a_{1g})^2$ $(6e_u)^4$	2.79 3.05 3.09	B	3.0-3.6
	$(6a_{2u})^2$ $(5e_g)^4$ $(7a_{1g})^2$	4.20 4.26 4.43	C	4.3-4.7

[a]The ground state electronic configuration for the $\mathbf{W_2O_7^{2-}}$ (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 $\mathbf{Cr_2O_7^{2-}}$ and $\mathbf{Mo_2O_7^{2-}}$ with D_{3d} symmetry.

[b]Numbers 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

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

[b]Numbers 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		

[a]The ground state electronic configuration for the $\mathbf{W_2O_7^-}$ (C_1, ^{2}A) anion (**2a** in Figure 4) is: $(37a)^2(38a)^2(39a)^2(40a)^2(41a)^2(42a)^2(43a)^1$.

[b]Numbers in parentheses represent the experimental uncertainties in the last digit.

Figure S1. Photoelectron spectra for $Cr_2O_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

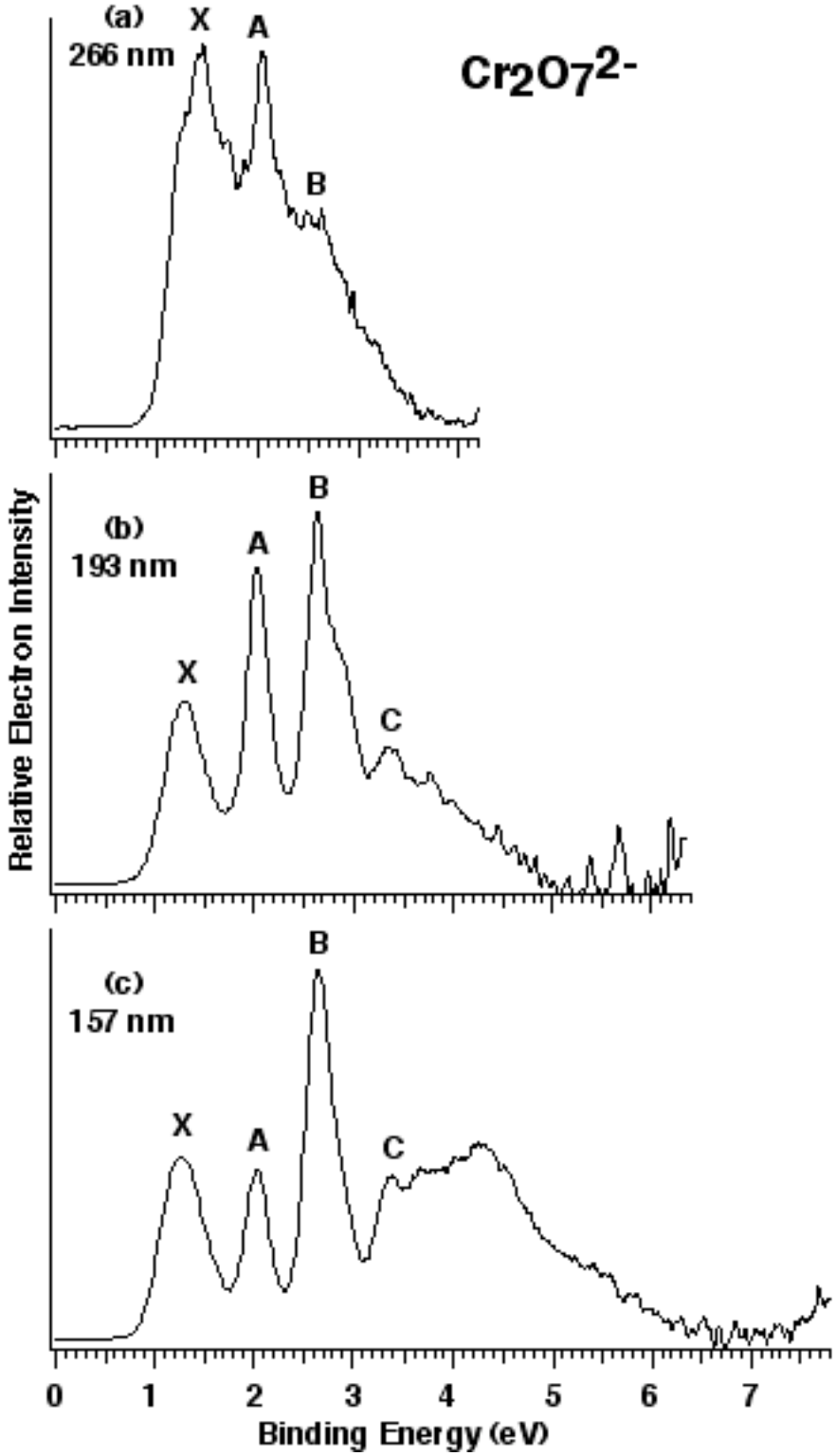

Figure S2. Photoelectron spectra for $Mo_2O_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

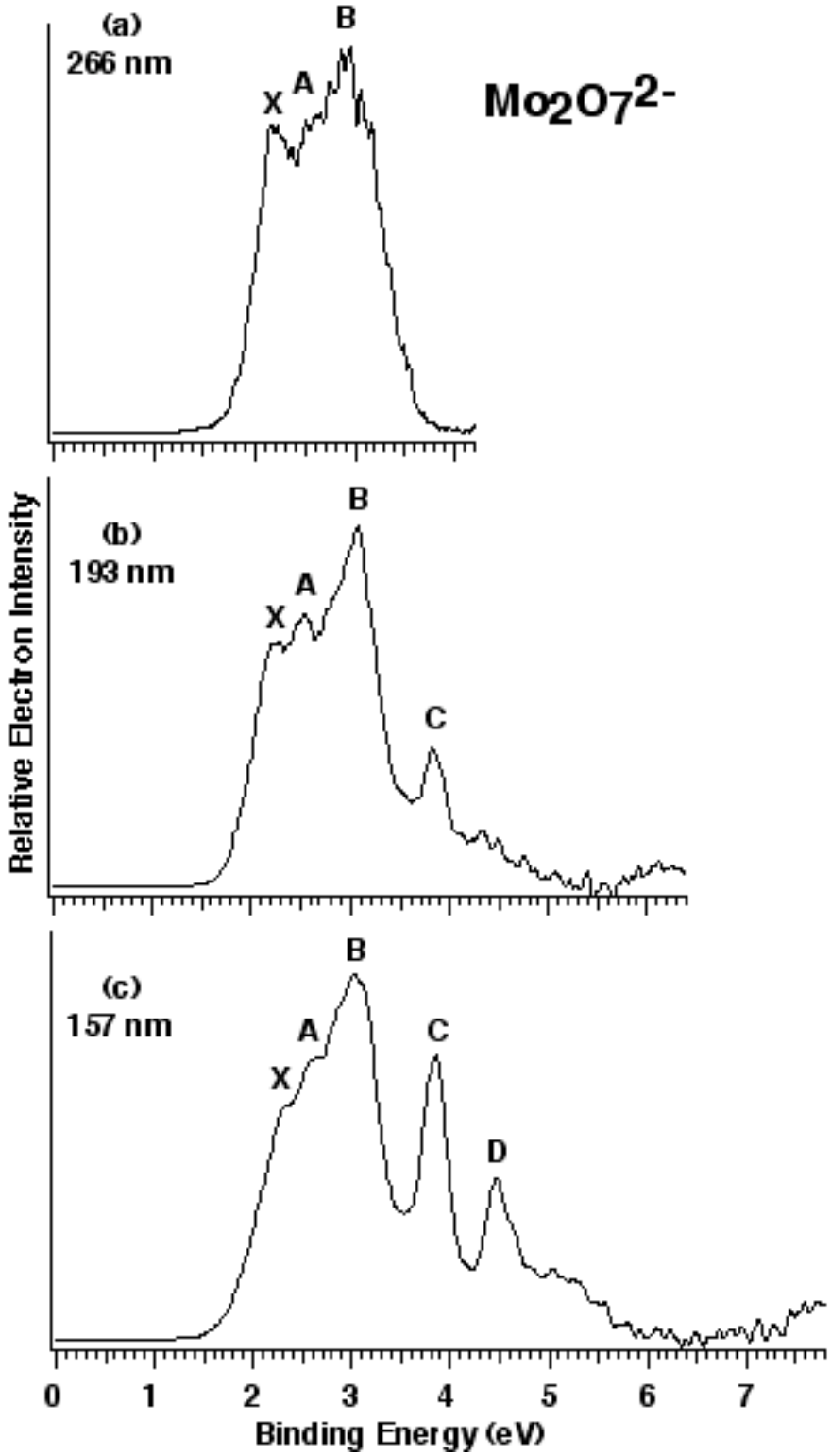

Figure S3. Photoelectron spectra for $W_2O_7^{2-}$ at (a) 193 nm and (b) 157 nm.

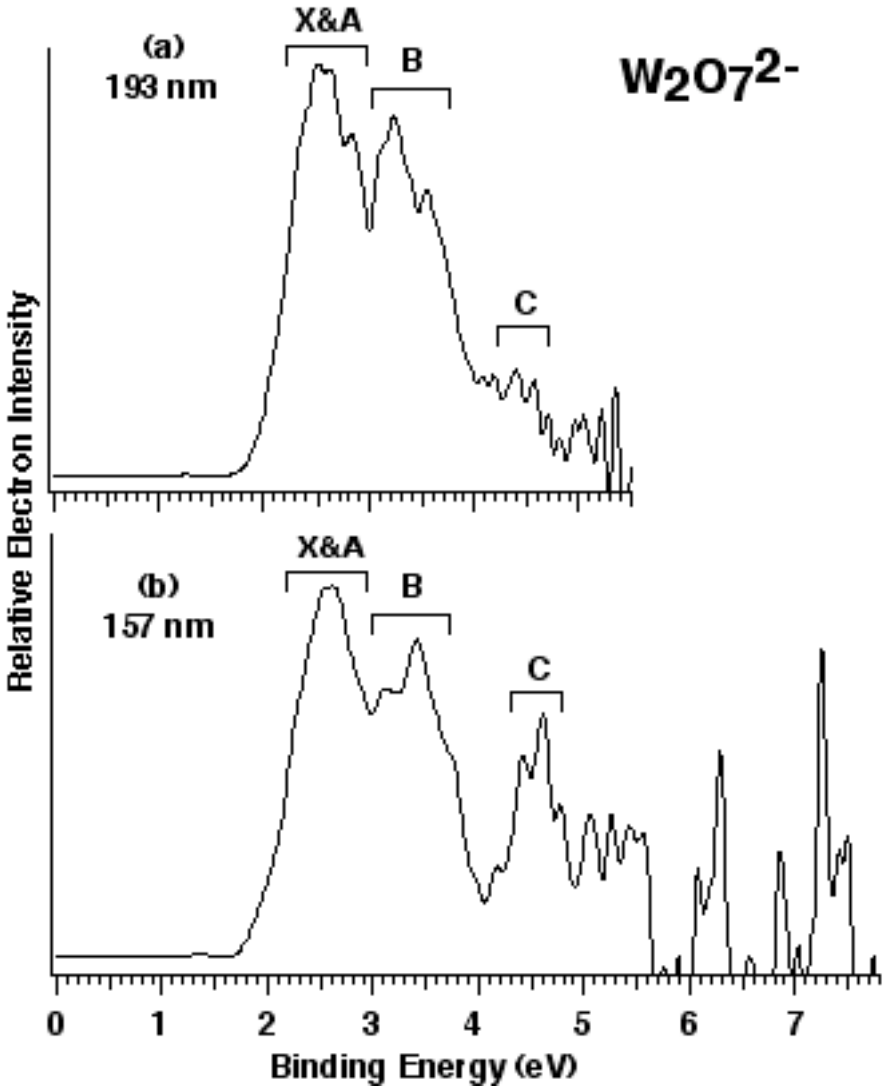

Figure S4. Photoelectron spectra for $CrMoO_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

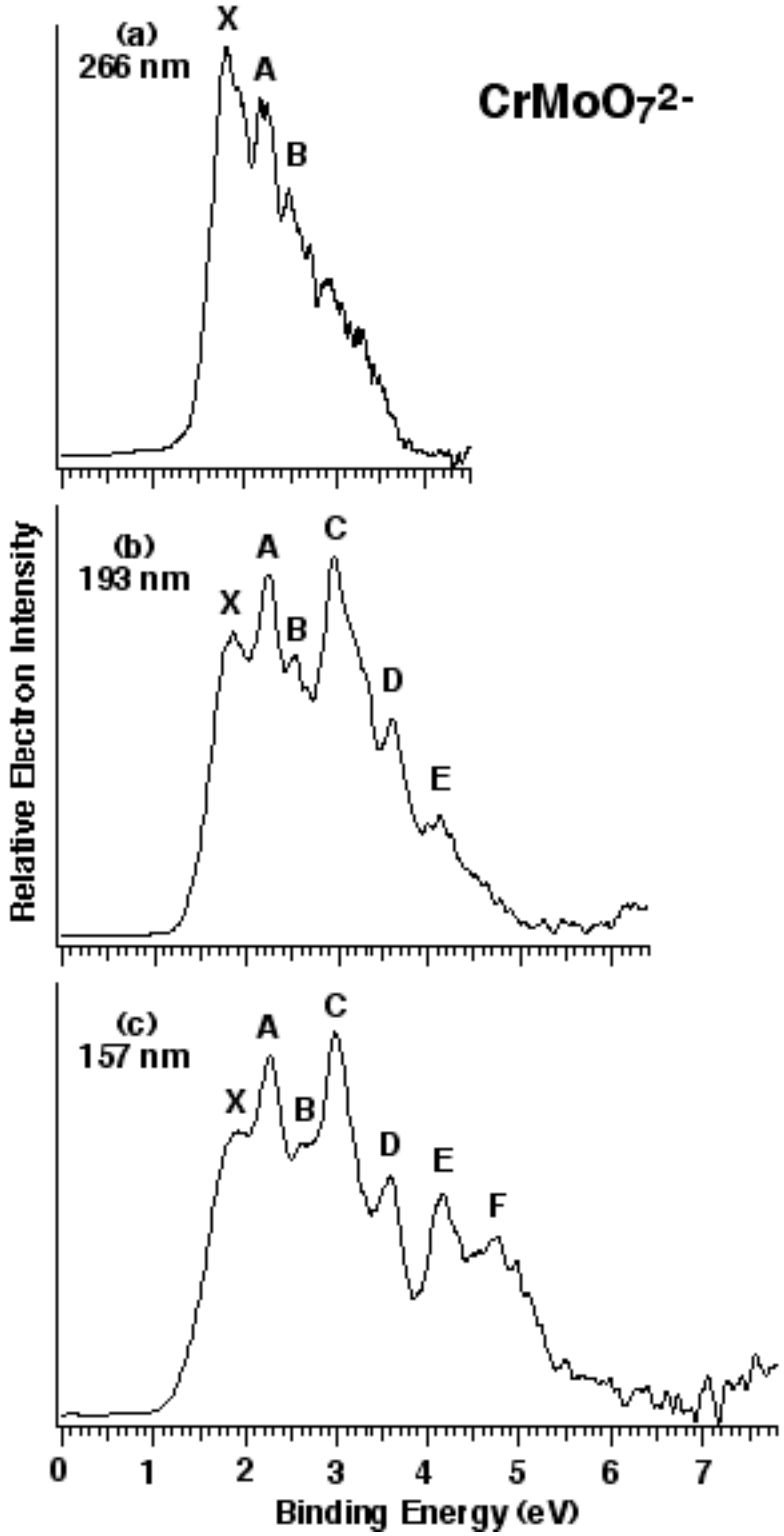

Figure S5. Photoelectron spectra for $CrWO_7^{2-}$ at (a) 266 nm, (b) 193 nm, and (c) 157 nm.

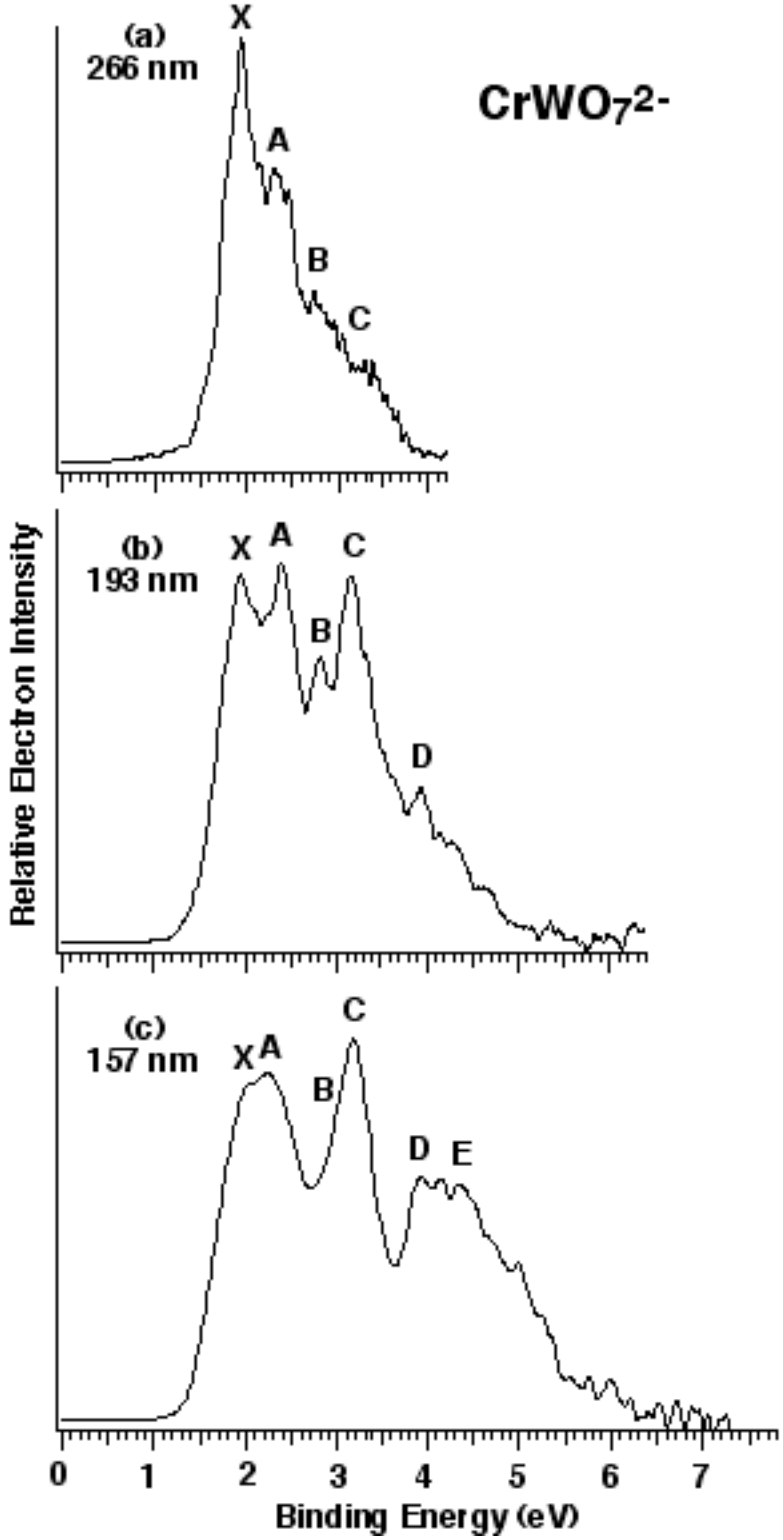

Figure S6. Photoelectron spectra for $MoWO_7^{2-}$ at (a) 193 nm and (b) 157 nm.