Supporting Information

Photoelectron imaging spectroscopic study and chemical-bonding analysis of VO_2^-, NbO_2^- and TaO_2^-

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Angular Distributions and the β Parameter

The photoelectron angular distribution (PAD), anisotropy parameter β (ranging from -1 to 2) could also exhibit qualitative fingerprint into the photo-detachment process from specific molecular orbital. As listed in Table 4, the HOMO orbitals have dominant orbital component in NbO_2^- {Nb (86s+3p+9d) + O (2s)} and TaO_2^- {Ta (87s+3p+8d) + O (2s)}. We can enumerate most possible combinations results of NbO_2^- and TaO_2^- for the hypothetical β-waves

NbO_2^- for β:

$$\beta \sim (0.88)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to d}_{1} + (0.09)\,\beta^{d\to f}_{0.8} \sim 1.86 \qquad (1)$$

$$\beta \sim (0.88)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to d}_{1} + (0.09)\,\beta^{d\to p}_{0.2} \sim 1.81 \qquad (2)$$

$$\beta \sim (0.88)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to s}_{0} + (0.09)\,\beta^{d\to f}_{0.8} \sim 1.83 \qquad (3)$$

$$\beta \sim (0.88)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to s}_{0} + (0.09)\,\beta^{d\to p}_{0.2} \sim 1.78 \qquad (4)$$

TaO_2^- for β:

$$\beta \sim (0.89)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to d}_{1} + (0.08)\,\beta^{d\to f}_{0.8} \sim 1.87 \qquad (1)$$

$$\beta \sim (0.89)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to d}_{1} + (0.08)\,\beta^{d\to p}_{0.2} \sim 1.83 \qquad (2)$$

$$\beta \sim (0.89)\,\beta^{s\to p}_{2} + (0.03)\,\beta^{p\to s}_{0} + (0.08)\,\beta^{d\to f}_{0.8} \sim 1.84 \qquad (3)$$

$$\beta \sim (0.78)\,\beta^{s\to p}_{2} + (0.02)\,\beta^{p\to s}_{0} + (0.20)\,\beta^{d\to p}_{0.2} \sim 1.79 \qquad (4)$$

Table S1

Natural localized molecular orbitals (NLMO) in MO_2^- (M = V, Nb and Ta) at the level of MP2 (the basis set of LANL2TZ for V, Nb and Ta, aug-cc-pVTZ for O).

Natural localized molecular orbitals (NLMO)		
Bond	Order	Component
V-O	No. 1	15.4% V($p^{1.00}d^{15.14}$) + 84.6% O($p^{1.00}$)
	No. 2	18.6% V($sp^{0.79}d^{1.86}$) + 81.4% O($sp^{2.55}$)
	No. 3	13.2% V($sp^{69.21}d^{99.99}$) + 86.8% O($sp^{99.99}d^{3.90}$)
Nb-O	No. 1	16.1% Nb($p^{1.00}d^{18.05}$) + 83.9% O($p^{1.00}$)
	No. 2	20.3% Nb($sp^{0.1}d^{6.57}$) + 79.7% O($sp^{3.44}$)
	No. 3	8.0% Nb($sp^{24.60}d^{24.26}$) + 92.0% O($sp^{24.3}6d^{0.07}$)
Ta-O	No. 1	15.0% Ta($p^{1.00}d^{11.33}$) + 85.0% O($p^{1.00}$)
	No. 2	17.4% Ta($sp^{0.21}d^{8.09}$) + 82.6% O($sp^{2.84}$)
	No. 3	8.1% Ta($sp^{20.42}d^{19.31}$) + 91.9% O($sp^{12.97}d^{0.04}$)

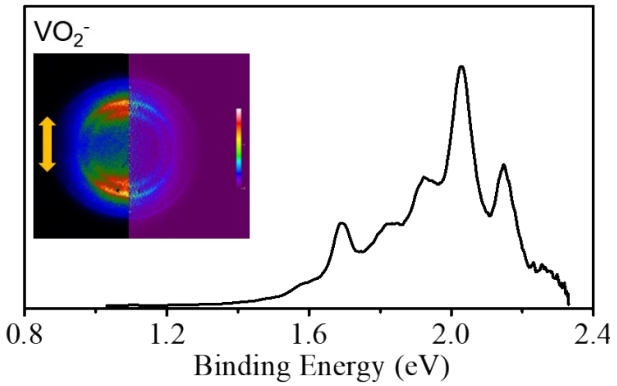

Fig. S1 Photoelectron images (left columns) and spectra (right columns) for VO_2^- obtained at 532 nm. The left side shows the raw photoelectron image (left) and the reconstructed one (right) after inverse Abel transformation. Laser polarization is vertical in the plane of the page.

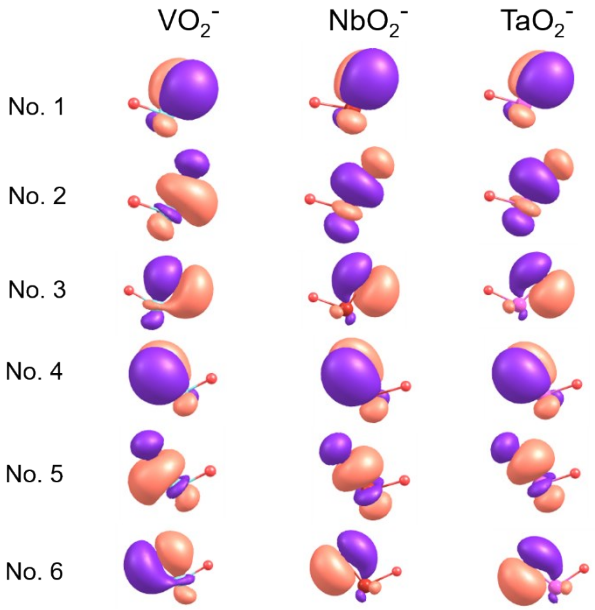

Fig. S2 NBOs in MO_2^- (M = V, Nb and Ta) at the level of MP2 (the basis set of LANL2TZ for V, Nb and Ta, aug-cc-pVTZ for O).