Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information for

Thermodynamic Insight Into AnO_2^+ Bonding from ThH^+/UH^+ Reactions Studied by Inductively Coupled Plasma Tandem Mass Spectrometry

Richard M Cox* Amanda R. Bubas, and Amanda D. French

Pacific Northwest National Laboratory, Richland, WA 99352 USA

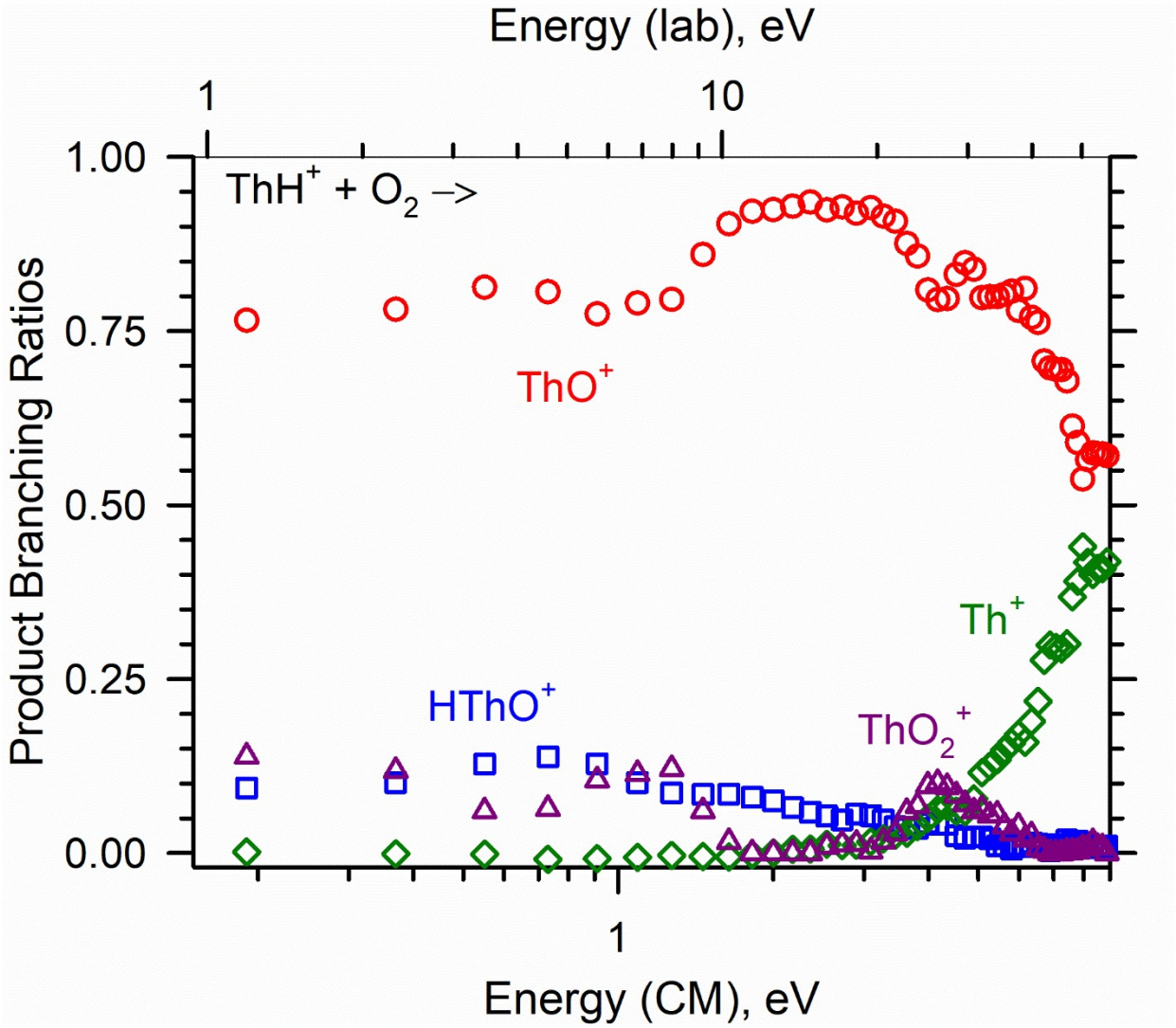

Figure S1. Product branching ratios for the reaction of $ThH^+ + O_2$ as a function of kinetic energy in the laboratory (upper x-axis) and the center-of-mass (lower x-axis).

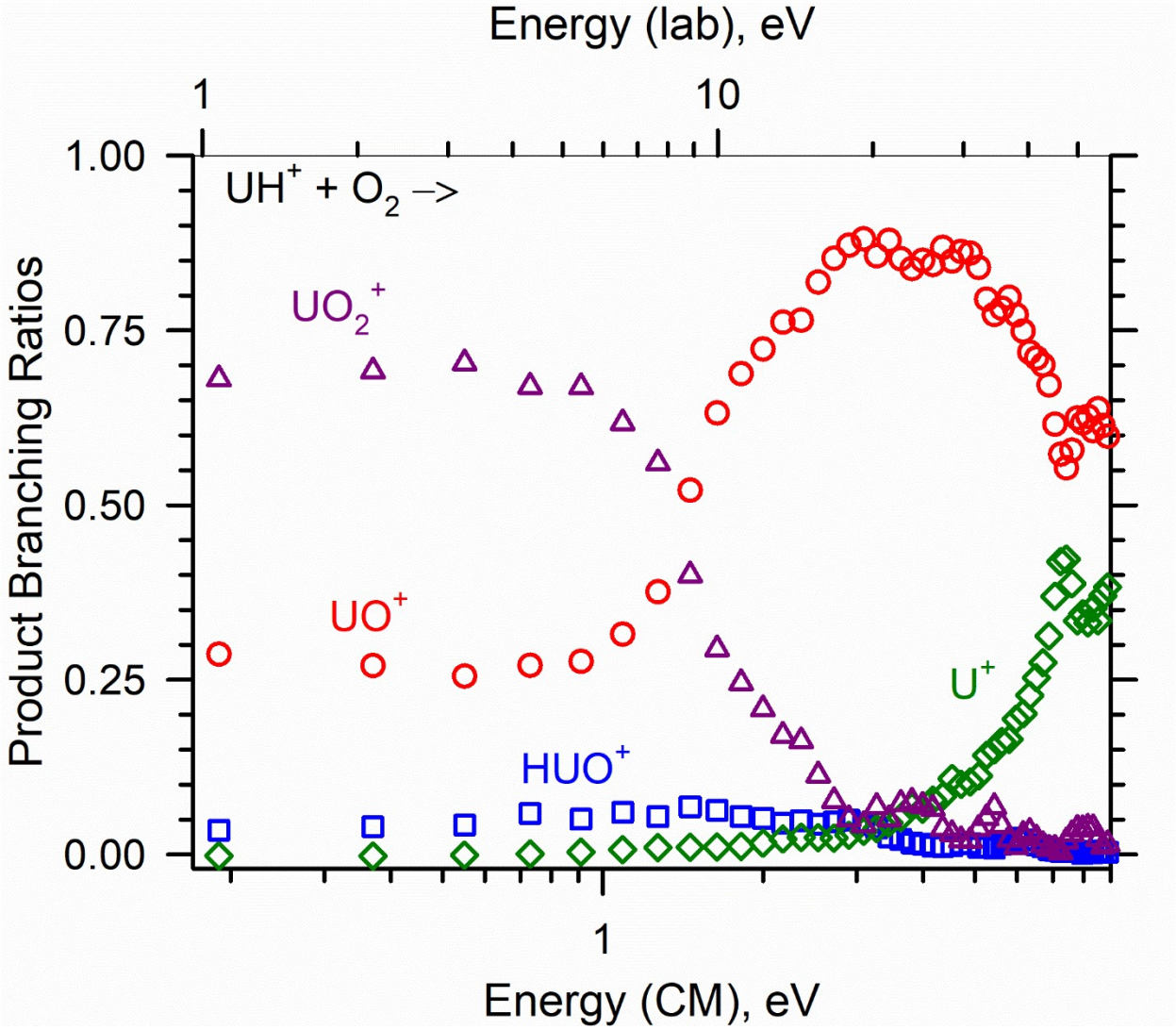

Figure S2. Product branching ratios for the reaction of $UH^+ + O_2$ as a function of kinetic energy in the laboratory (upper x-axis) and the center-of-mass (lower x-axis).

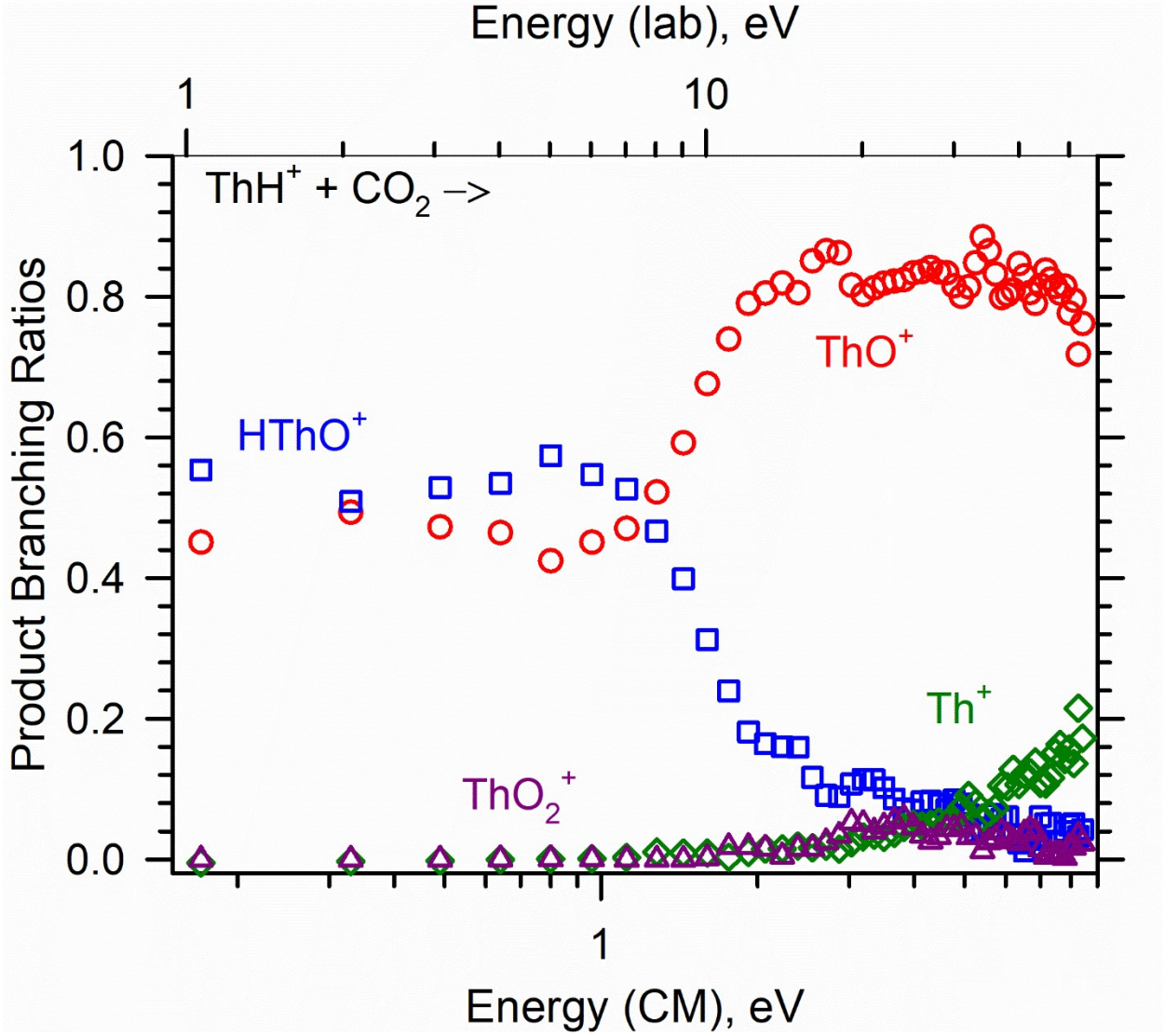

Figure S3. Product branching ratios for the reaction of $ThH^+ + CO_2$ as a function of kinetic energy in the laboratory (upper x-axis) and the center-of-mass (lower x-axis).

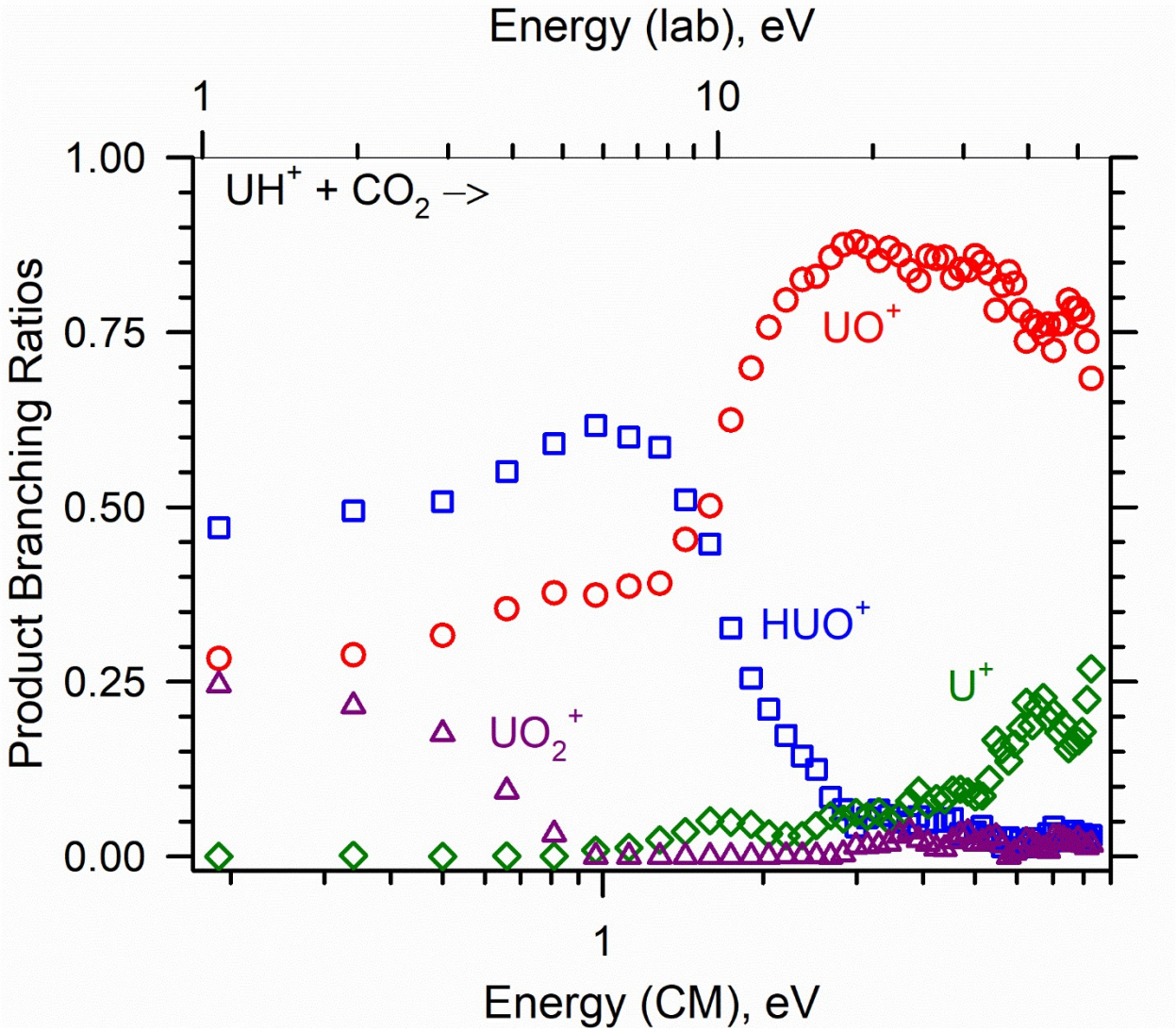

Figure S4. Product branching ratios for the reaction of $UH^+ + CO_2$ as a function of kinetic energy in the laboratory (upper x-axis) and the center-of-mass (lower x-axis).

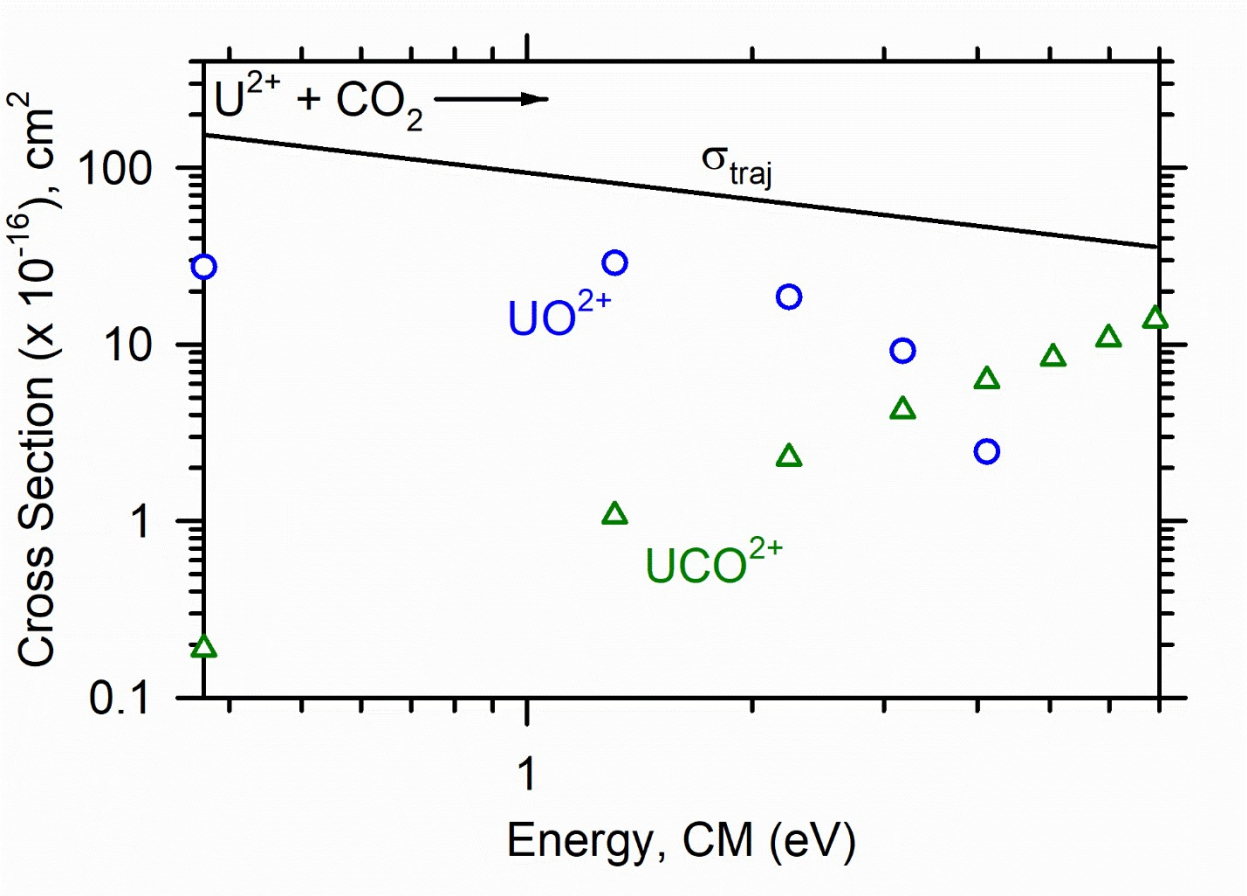

Figure S5. The absolute reaction cross section of $U^{2+} + CO_2$ as a function of kinetic energy in the center-of-mass frame. Individual products are UO^{2+} (blue circles) and UCO^{2+} (green triangles). The Su-Chesnavich semi-classical trajectory (σ_{traj}) collision limit is represented by a solid black line.

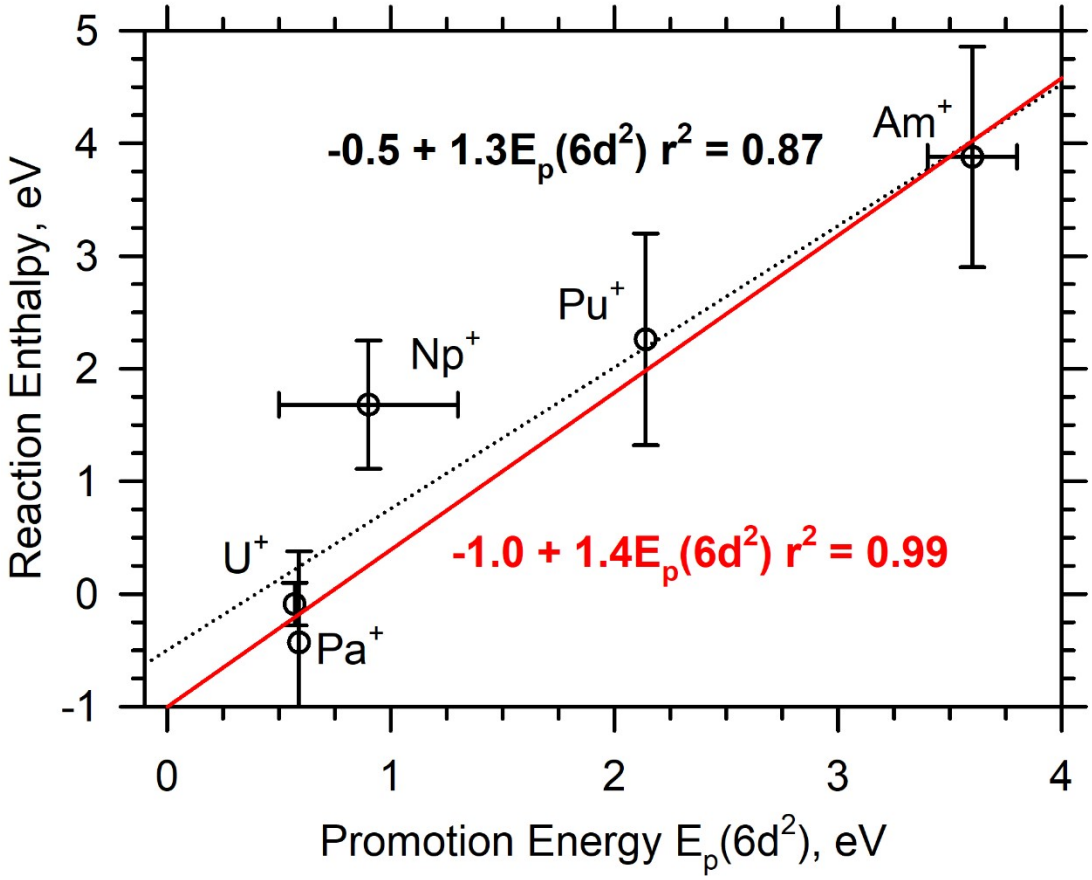

Figure S6. The correlation between $E_p(6d^2)$ and the reaction 10 enthalpy calculated using the values found in Table 4 and equation 17. The solid red line represents the least square linear regression trend line omitting NpO_2^+ ($-1.0 + (1.4 \pm 0.1)E_p(6d^2)$, $r^2 = 0.99$). The dotted black line represents the trend including NpO_2^+, see Figure 5 ($-0.5 + (1.3 \pm 0.3)E_p(6d^2)$, $r^2 = 0.87$).

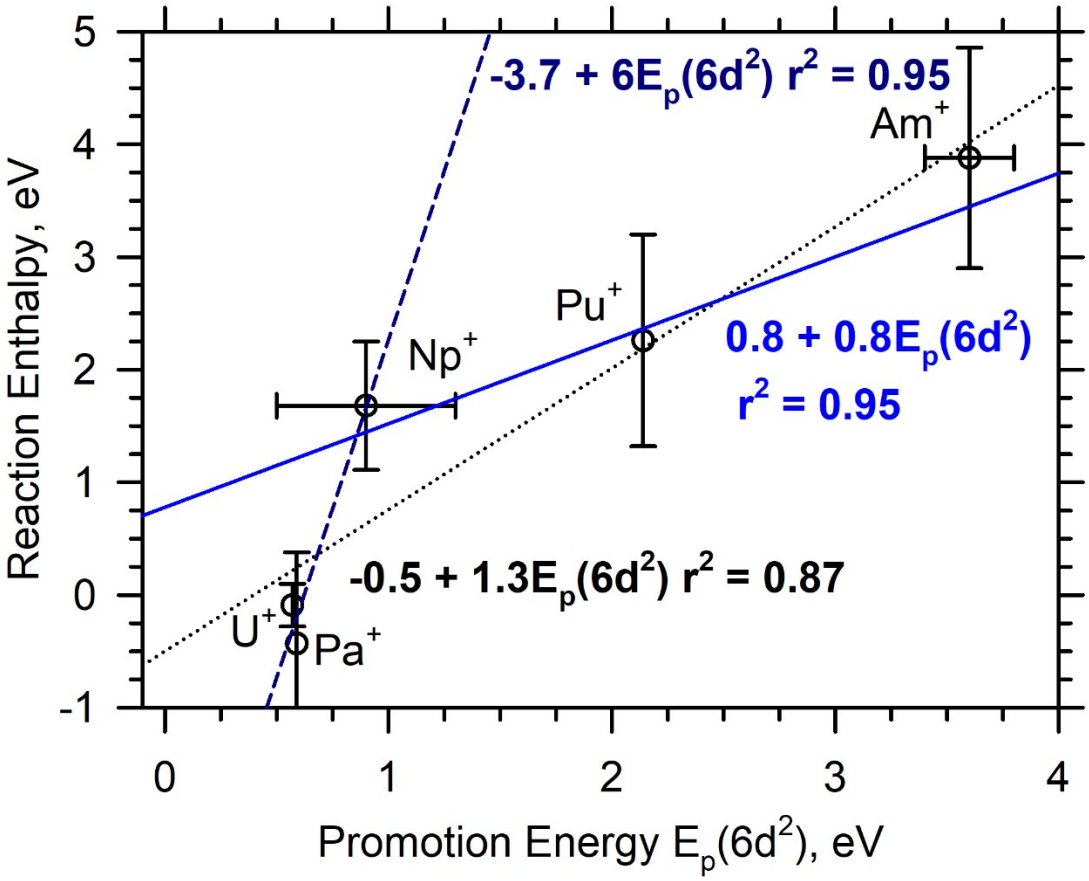

Figure S7. The correlation between Ep(6d2) and the reaction 10 enthalpy calculated using the values found in Table 4 and equation 17. The dashed dark blue line represents the least square linear regression trend line for PaO_2^+ - NpO_2^+ (-3.7+ (6 ± 1)Ep(6d^2), r2 = 0.95). The solid blue line represents the least square linear regression trend line for NpO_2^+ - AmO_2^+ (0.8+ (0.8 ± 0.2)Ep(6d^2), r2 = 0.95). The dotted black line represents the trend including NpO_2^+, see Figure 5 (-0.5 + (1.3 ± 0.3)E$_p$(6d^2), r^2 = 0.87).

Reaction S1

$An^+ + O_2 \rightarrow AnO^+ + O$

Reaction S2

$An^{2+} + O_2 \rightarrow AnO^{2+} + O$

Reaction S3

$AnH^+ + O_2 \rightarrow AnO^+ + OH$

Reaction S4

$An^+ + O_2 \rightarrow HAnO^+ + O$

Reaction S5

$An^+ + O_2 \rightarrow AnO_2^+ + H$

Reaction S6

$AnO^+ + O_2 \rightarrow AnO_2^+ + O$

Reaction S7

$An^+ + CO_2 \rightarrow AnO^+ + CO$

Reaction S8

$An^{2+} + CO_2 \rightarrow AnO^{2+} + CO$

Reaction S9

$AnH^+ + CO_2 \rightarrow AnO^+ + OCH$

Reaction S10

$AnH^+ + CO_2 \rightarrow HAnO^+ + CO$

Reaction S11

$AnH^+ + CO_2 \rightarrow AnO_2^+ + CH$

Reaction S12

$AnO^+ + CO_2 \rightarrow AnO_2^+ + CO$

Table S1. Reaction enthalpies ($\Delta_rH^\circ_0$) of reactions listed in Table 2 (in eV).

	$\Delta_rH^\circ_0$(S1)[a]	$\Delta_rH^\circ_0$(S2)[b]	$\Delta_rH^\circ_0$(S3)[c]	$\Delta_rH^\circ_0$(S4)[d]	$\Delta_rH^\circ_0$(S5)[c]	$\Delta_rH^\circ_0$(S6)[e]
Th	-3.46 ± 0.14	-3.48 ± 0.83	-5.45 ± 0.16	≤ -0.34	-5.88 ± 0.16	0.17 ± 0.06
U	-2.77 ± 0.09	-2.21 ± 0.47	-4.87 ± 0.15	≤ -0.34	-7.99 ± 0.19	-2.45 ± 0.12
	$\Delta_rH^\circ_0$(S7)[f]	$\Delta_rH^\circ_0$(S8)[g]	$\Delta_rH^\circ_0$(S9)[c]	$\Delta_rH^\circ_0$(S10)[h]	$\Delta_rH^\circ_0$(S11)[c]	$\Delta_rH^\circ_0$(S12)[i]
Th	-3.12 ± 0.14	-3.14 ± 0.83	-2.48 ± 0.16	≤ 0	2.02 ± 0.16	0.51 ± 0.06
U	-2.43 ± 0.09	-1.87 ± 0.47	-1.90 ± 0.15	≤ 0	-0.09 ± 0.19	-2.11 ± 0.12

a. $\Delta_rH^\circ_0$(S1) = D_0(O-O) = 5.11 eV[1] – D_0(An^+-O) = 8.57 ± 0.14 eV[2] or 7.88 ± 0.09 eV[3]
b. $\Delta_rH^\circ_0$(S2) = D_0(O-O) = 5.11 eV[1] – D_0(An^{2+}-O)[4] = 8.59 ± 0.83 eV or 7.32 ± 0.47 eV
c. See Table 4
d. $\Delta_rH^\circ_0$(S4) ≤ D_0(OC-O) = 5.45 eV - D_0(O-O) = 5.11 eV[1] = -0.34 eV
e. $\Delta_rH^\circ_0$(S6) = D_0(O-O) = 5.11 eV[1] – D_0(OAn^+-O) = 4.94 ± 0.06 eV[5] or 7.56 ± 0.12 eV[6]
f. $\Delta_rH^\circ_0$(S7) = D_0(OC-O) = 5.45 eV[1] – D_0(An^+-O) = 8.57 ± 0.14 eV[2] or 7.88 ± 0.09 eV[3]
g. $\Delta_rH^\circ_0$(S8) = D_0(OC-O) = 5.45 eV[1] – D_0(An^{2+}-O)[4] = 8.59 ± 0.83 eV or 7.32 ± 0.47 eV
h. Exothermic reactions observed in Figures 3 and 4.
i. $\Delta_rH^\circ_0$(S12) = D_0(OC-O) = 5.45 eV[1] – D_0(OAn^+-O) = 4.94 ± 0.06 eV[5] or 7.56 ± 0.12 eV[6]

Table S2. Promotion energies, $E_p(6d^n)$ and AnO_x^+ BDEs (in eV).[a]

	E_p(6d)	E_p($6d^2$)	D_0(An^+-O)	D_0(OAn^+-O)
Th^+	0.00	0.00	8.57 ± 0.14[b]	4.87 ± 0.04[c]
Pa^+	0.10	0.59	8.29 ± 0.52	8.08 ± 0.30
U^+	0.04	0.57	8.02 ± 0.14[d]	7.56 ± 0.12[e]
Np^+	0.00	0.9 ± 0.4	7.88 ± 0.10	6.32 ± 0.23
Pu^+	1.08	2.14	6.75 ± 0.20	5.28 ± 0.39
Am^+	1.76	3.6 ± 0.2	5.80 ± 0.29	4.25 ± 0.58

a. Unless noted otherwise, Ref. [4]
b. Ref. [2]
c. Ref. [5]
d. Ref. [3]
e. Ref. [6]

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