Supporting Material

"Quantum Chemical Calculations of Reduction Potentials of $\text{AnO}_2^{2+}/\text{AnO}_2^+$ (An = U, Np, Pu, Am) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ Couples"

Satoru Tsushima, Ulf Wahlgren, and Ingmar Grenthe

Table S1 The metal-oxygen bond distances in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$ and $[\text{An}(\text{H}_2\text{O})_5]^{2+/+}$ complexes (An=U, Np, Pu, Am) optimized at the UMP2/6-311+G* levels of theory (unit in Ångstrom).

			ECP ^{a)}	M-Oax	M-Oeq	
Fe	[Fe(H ₂ O) ₆] ³⁺	C _I	Fe	2.0356, 2.0356, 2.0356, 2.0354, 2.0354, 2.0355		
	[Fe(H ₂ O) ₆] ²⁺		Fe	2.1382, 2.1377, 2.1375, 2.1379, 2.1374, 2.1371		
U	[UO ₂ (H ₂ O) ₅] ²⁺	D _{5h}	U(SC)	1.7623	2.4429	
			U(SC), O	1.7685	2.4560	
	C _I		U(SC)	1.8083	2.5064	
			U(SC), O	1.8118	2.5264	
		U(SC)	1.7629, 1.7629	2.4429, 2.4426, 2.4427, 2.4431, 2.4432		
		U(SC), O	1.7685, 1.7685	2.4558, 2.4555, 2.4556, 2.4561, 2.4562		
		U(LC)	1.7561, 1.7561	2.4651, 2.4650, 2.4650, 2.4652, 2.4653		
		U(SC)	1.8078, 1.8078	2.5081, 2.5081, 2.5082, 2.5082, 2.5083		
	[UO ₂ (H ₂ O) ₅] ⁺	U(SC), O	1.8119, 1.8119	2.5265, 2.5257, 2.5253, 2.5258, 2.5265		
		U(LC)	1.8038, 1.8039	2.5295, 2.5289, 2.5298, 2.5291, 2.5301		
Np	[NpO ₂ (H ₂ O) ₅] ²⁺	D _{5h}	Np(SC)	1.7324	2.4246	
	Np(SC), O		1.7376	2.4369		
	Np(SC)		1.7681	2.4891		
	Np(SC), O		1.7708	2.5084		
	[NpO ₂ (H ₂ O) ₅] ⁺	C _I	Np(SC)	1.7325, 1.7324	2.4243, 2.4244, 2.4248, 2.4254, 2.4256	
			Np(LC)	1.7326, 1.7326	2.4505, 2.4514, 2.4525, 2.4524, 2.4511	
			Np(SC)	1.7687, 1.7686	2.4911, 2.4890, 2.4896, 2.4898, 2.4888	
			Np(LC)	1.7721, 1.7721	2.5201, 2.5205, 2.5212, 2.5212, 2.5205	
Pu	[PuO ₂ (H ₂ O) ₅] ²⁺	D _{5h}	Pu(SC)	1.7067	2.4053	
			Pu(SC), O	1.7111	2.4196	
			Pu(LC)	1.7328	2.5067	
			Pu(SC)	1.7397	2.4945	
			[PuO ₂ (H ₂ O) ₅] ⁺	Pu(SC), O	1.7409	2.5198
				Pu(LC)	1.7642	2.6245
	[PuO ₂ (H ₂ O) ₅] ²⁺	C _I		Pu(SC)	1.7066,1.7073	2.4050, 2.4050, 2.4050, 2.4052, 2.4052
				Pu(LC)	1.7318, 1.7323	2.5063, 2.5069, 2.5072, 2.5076, 2.5067
			Pu(SC)	1.7392, 1.7392	2.4967, 2.4951, 2.4914, 2.4907, 2.4938	
			Pu(LC)	1.7643, 1.7641	2.6372, 2.6333, 2.6185, 2.6141, 2.6255	
Am	[AmO ₂ (H ₂ O) ₅] ²⁺	D _{5h}	Am(SC)	1.7143	2.4324	
			Am(SC), O	1.7167	2.4477	
			Am(SC)	1.7126	2.5084	
			Am(SC), O	1.7147	2.5310	
	[AmO ₂ (H ₂ O) ₅] ²⁺	C _I	Am(SC)	1.7143, 1.7144	2.4329, 2.4343, 2.4339, 2.4329, 2.4318	
			Am(SC)	1.7122, 1.7124	2.5096, 2.5096, 2.5096, 2.5096, 2.5096	

a) SC: small core ECP (60 core electrons), LC: large core ECP (78 core electrons).

Table S2 Calculated entropy S, constant volume molar heat capacity C_v , thermal correction to enthalpy and to Gibbs energy. Values in parenthesis are experimental value.

	S (J/mol·K)	S(V,II)-S(VI,III) (J/mol·K)	C_v (J/mol·K)	Thermal correction to enthalpy	Thermal correction to Gibbs energy
H ₂	130.1(130.680±0.003)		20.8	0.013773 a.u.	-0.001000 a.u.
H ₂ O	188.0(188.835±0.01)		25.1	0.026811 a.u.	0.005457 a.u.
H ₃ O ⁺	202.0		27.9	0.040665 a.u.	0.017727 a.u.
Fe ³⁺ (H ₂ O) ₆	441.4(-293.3aq)	75.1	182.8	0.179692 a.u.	0.129522 a.u.
Fe ²⁺ (H ₂ O) ₆	516.5(-113.4aq)	(179.9aq)	335.2	0.177381 a.u.	0.118730 a.u.
UO ₂ ²⁺ (H ₂ O) ₅	489.4 (-98.2±3.0aq)	65.1	206.2	0.157340 a.u.	0.101768 a.u.
UO ₂ ⁺ (H ₂ O) ₅	554.5 (-25.0±8.0aq)	(73.2aq)	231.7	0.155784 a.u.	0.092813 a.u.
NpO ₂ ²⁺ (H ₂ O) ₅	518.1 (-92.4±10.7aq)	74.1	204.9	0.156029 a.u.	0.097196 a.u.
NpO ₂ ⁺ (H ₂ O) ₅	592.2 (-45.9±10.5aq)	(46.5aq)	245.0	0.157006 a.u.	0.089761 a.u.
PuO ₂ ²⁺ (H ₂ O) ₅	529.3 (1.5±30.0aq)	72.9	214.8	0.155759 a.u.	0.095646 a.u.
PuO ₂ ⁺ (H ₂ O) ₅	602.2 (-71.2±21.2aq)	(72.7aq)	235.5	0.153014 a.u.	0.084631 a.u.

Table S3 Breakdown of calculated entropy values of gas phase $\text{AnO}_2^{2+/+}$ ions (J/mol·K)

U(VI)	
Electronic	0.0
Translational	182.2
Rotational	105.8
Vibrational	201.4
<u>Total</u>	<u>489.4</u>

U(V)	
Electronic	5.8
Translational	182.2
Rotational	106.7
Vibrational	259.9
<u>Total</u>	<u>554.5</u>

Np(VI)	
Electronic	5.8
Translational	182.1
Rotational	124.8
Vibrational	205.3
<u>Total</u>	<u>518.1</u>

Np(V)	
Electronic	9.1
Translational	182.1
Rotational	125.7
Vibrational	275.2
<u>Total</u>	<u>592.2</u>

Pu(VI)	
Electronic	9.1
Translational	182.3
Rotational	125.4
Vibrational	212.5
<u>Total</u>	<u>529.3</u>

Pu(V)	
Electronic	11.5
Translational	182.3
Rotational	126.5
Vibrational	281.8
<u>Total</u>	<u>602.2</u>