Supplementary Information for

Exploring the kinetics of actinyl-EDTA reduction by ferrous iron using quantum-mechanical calculations

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Test of density functionals and basis sets

We performed the reduction kinetics calculation using B3LYP hybrid functional,[1, 2] which has proven to produce reliable results for actinide complexes.[3-5] However, in order to show the influence of the selected density functionals, we tested several density functionals here and compared the results. In addition to B3LYP (hybrid), we tested PBE0 (hybrid)[6] and M06L (meta-GGA).[7] From the results, the positions of energy minima and activation energy barriers were almost the same (differences <0.25 Å, Table S1). However, there are some changes in the E_a (activation energies of dehydration) values. Using the PBE0 functional results in an increase in E_a by 7 kJ/mol in the forward reaction (OSC to ISC) and 8 kJ/mol in the backward reaction (ISC to OSC). Normalized total energy values for the ISC and OSC are close to the B3LYP results with less than 13 kJ/mol differences. M06L results in a similar value for $E_{a,back}$, but more significant change (-9 kJ/mol) in E_a than using the PBE0 functional.

In addition, two different basis sets were tested at the B3LYP level for actinide elements (An = U, Np, and Pu) to see if there is a significant energy change due to the change of basis sets. With LANL2DZ[8, 9] on lighter elements, we compared Stuttgart relativistic small-core (RSC)[10, 11] vs. Stuttgart relativistic large-core (RLC)[12] basis sets with their corresponding pseudopotentials. The same as in the density functional test, the position of energy minima at ISC and OSC are very close to each other (Table S2). E_a values are very similar, but $E_{a,back}$ increased by 13 kJ/mol. Previous studies that compared Stuttgart RSC and RLC basis sets showed that Stuttgart RSC produces more comparable dissociation energies with experiment,[13] and Stuttgart RLC yields poor geometries (too short bonds) and frequency results for UO_2^{2+}.[14, 15]

However, there are no reliable experimental data to gauge those results. Therefore, we chose B3LYP in combination with Stuttgart RSC basis sets (for Fe, U, Np, and Pu) and LANL2DZ (for all lighter elements) in this study, which has been used in many previous studies and proven to produce comparable results with experiments.[13, 16, 17]

Table S1. Calculated energy barriers (dG (kJ/mol)) for the OSC to ISC transition of $[UO_2(edta)]^{2-}$ reduction by ferrous iron using different density functionals. λ represents the distance between the two energy minima (ISC and OSC).

	E_a (kJ/mol)	$E_{a,back}$ (kJ/mol)	ISC minimum U-Fe distance (Å)	OSC minimum U-Fe distance (Å)	λ (Å)
B3LYP	60.5	49.7	4	6.75	2.75
PBE0	67.4	57.7	4	6.75	2.75
M06L	51.8	48.6	4	6.8	2.8

Table S2. Calculated energy barriers (dG (kJ/mol)) for the OSC to ISC transition of $[UO_2(edta)]^{2-}$ reduction by ferrous iron using two different basis sets. λ represents the distance between the two energy minima (ISC and OSC).

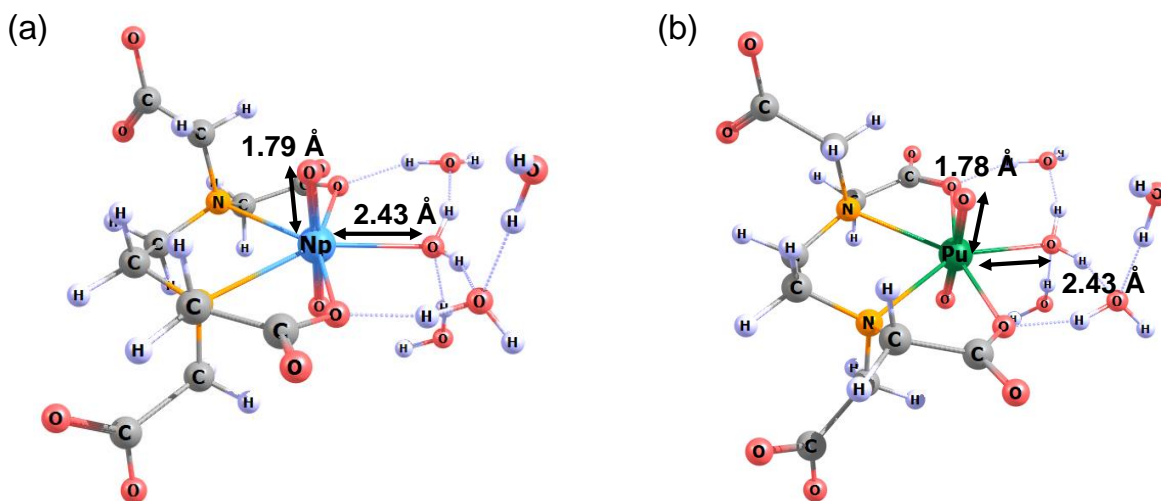|	E_a (kJ/mol)	$E_{a,back}$ (kJ/mol)	ISC minimum U-Fe distance (Å)	OSC minimum U-Fe distance (Å)	λ (Å)
Stuttgart RSC ECP	60.5	49.7	4	6.75	2.75
Stuttgart RLC ECP	59.6	56.7	4.25	7	2.75

Fig. S1. Optimized geometries of (a) $[NpO_2(edta)]^{2-}$ and (b) $[PuO_2(edta)]^{2-}$ before reaction with the reductant. White-H, gray-C, red-O, orange-N, blue-Np, and green-Pu. The dotted gray lines indicate hydrogen bonds.

Spin density changes and the effect of spin contamination

The expected and calculated values of the spin and $<S^2>$ for An(VI)-EDTA and Fe(II) before and after the electron transfer were calculated (Table S3). The total spin densities are the same when compared $<S>$ values before and after the electron transfer. Spin contamination was calculated by comparing calculated $<S^2>$ with expected values using S as the sum of spins for Fe and the actinide ions before and after the redox event and then calculating $S(S+1)$. Negligible differences were obtained for most model setups except for the Np(V)-Fe(III) system. The effect of spin contamination in DFT methods is less significant than in Hartree-Fock calculations.[18, 19]

Table S3. Comparison of the expected and calculated values of the spin and $<S^2>$ for An(VI)-EDTA and Fe(II) before and after the electron transfer.

Spin density	U 0(U)/ 4(Fe)	Np -1(Np)/ 4(Fe)	-2(Np)/ 5(Fe)	Pu -2(Pu)/ 4(Fe)	-3(Pu)/ 5(Fe)
	Before ET	Before ET	After ET	Before ET	After ET
Expected sum of spin	(0+4) 4	(-1 + 4) 3	(-2 + 5) 3	(-2 + 4) 2	(-3 + 5) 2
Sum of spin (Bader)	(0+4.00) 4	(-0.90 + 3.90) 3	(-1.65 + 4.65) 3	(-2.00 + 4.00) 2	(-3.00 + 4.99) 2
Sum of spin (Mulliken)	(0+4) 4	(-0.94 + 3.94) 3	(-1.66 + 4.66) 3	(-2.00 + 4.00) 2	(-2.99 + 4.99) 2
Expected $S(S+1)$	6.0	5.25	6.75	4.0	5.0
Calculated $<S^2>$ by Gaussian	6.0	4.8	5.8	4.1	5.1
% difference of $<S^2>$ - $S(S+1)$	0	-8.6	-14.1	2.5	2.0

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