

Supporting Information for

## Binding of Pertechnetate to Uranyl(VI) in Aqueous Solution. A Density-Functional Molecular Dynamics Study.

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### 1. Details of Construction and Validation of the Tc Pseudopotential

For technetium, a semicore (or small-core) pseudopotential was constructed following the procedure adopted previously for other transition-metal nuclei.<sup>1</sup> A relativistic atomic reference calculation was performed for the  $[1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}] 4s^2 4p^6 4d^5$  state, and a pseudopotential was created for the core in brackets, using cutoff radii of 2.2, 2.2, and 2.0 a.u. for the  $s$ ,  $p$ , and  $d$  channels, respectively.<sup>2</sup> Since this atomic calculation was performed for a  $Tc^{2+}$  state, the resulting pseudopotential is thus designed for technetium in high oxidation states.

Static optimizations and numeric frequency calculations were performed in the in the gas phase at the BLYP level, employing the CPMD program and the parameters detailed in reference 7 of the main paper (denoted CP-opt), and validated against experiment or SDD/6-31G\* computations using Gaussian 03<sup>3</sup> with the same functional (SDD denoting the Stuttgart-Dresden relativistic effective core potential, ECP, for Tc,<sup>4</sup> see below for more details). Some representative results are summarized in Tables S1 and S2.

**Table S1:** Tc-O bond distance (in Å) and harmonic vibrational frequencies (in  $cm^{-1}$ ) for  $TcO_4^-$  (BLYP level).

Parameter	CP-opt <sup>a</sup>	SDD/6-31G*	Expt. [reference]
$r(Tc-O)$	1.738	1.755	1.676 [5]
$\nu_3 (T_2)$	880	887	912 [6]
$\nu_1 (A_1)$	889	877	912
$\nu_4 (T_2)$	308	321	325
$\nu_2 (E)$	270	301	-

<sup>a</sup>Box size 9.8692 Å

**Table S2:** Bond distance (in Å), bond angles (in degrees) and relative energies (in kcal/mol) for *cis*- and *trans*-TcO<sub>2</sub>F<sub>4</sub><sup>-</sup> (BLYP level).

Complex	Parameter	CP-opt <sup>a</sup>	SDD/6-31G*	Expt. <sup>b</sup>
<i>cis</i> (C <sub>2v</sub> )	<i>r</i> (Tc-O)	1.707	1.736	1.660(4)
	<i>r</i> (Tc-F <sub>ax</sub> )	1.917	1.926	1.876(3)
	<i>r</i> (Tc-F <sub>eq</sub> )	1.975	1.971	1.986(3)
	<i>a</i> (O-Tc-O)	101.3	102.2	102.5(3)
	<i>a</i> (F <sub>ax</sub> -Tc-F <sub>ax</sub> )	168.7	167.7	164.2(3)
<i>trans</i> (D <sub>4h</sub> )	<i>r</i> (Tc-O)	1.765	1.788	-
	<i>r</i> (Tc-F <sub>ax</sub> )	1.910	1.922	-
	<i>E</i> <sub>rel</sub> <sup>b</sup>	29.0	25.4	-

<sup>a</sup>Box size 13.67 Å. <sup>b</sup>From reference 7. <sup>c</sup>Relative to *cis* isomer.

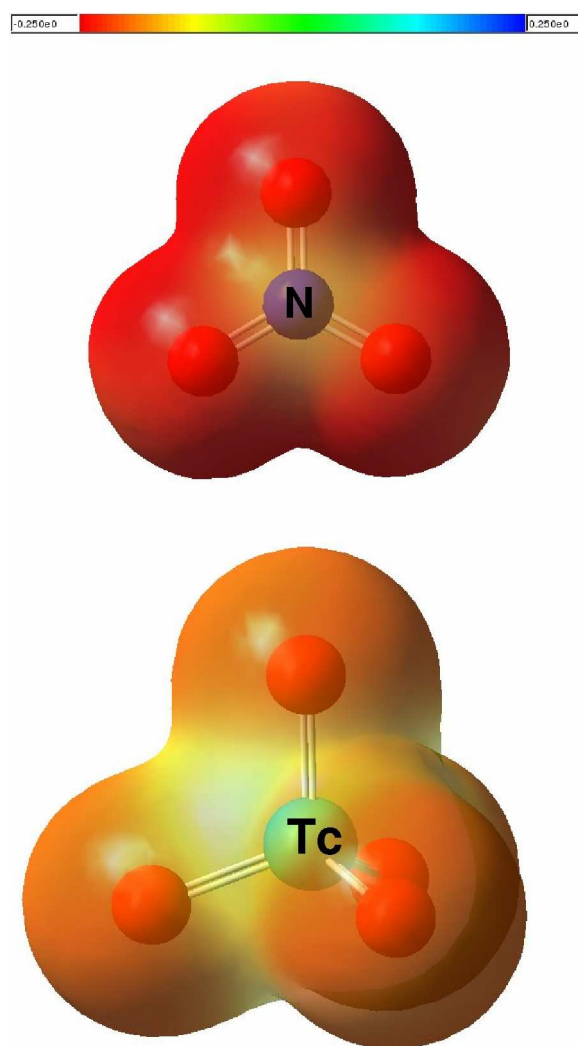
By and large, the SDD/6-31G\* results are reasonably well reproduced by the CP-opt data. No improvement could be brought about by choosing other cutoff radii for the *s,p,d* channels during construction of the Tc pseudopotential. Compared to experiment, the BLYP functional displays the typical<sup>8</sup> overestimation of bond distances, which can be improved by using other functionals, e.g. BP86 (data not shown). The BLYP functional has been used because of its good performance to describe the properties of liquid water,<sup>9</sup> as well as the dynamics, thermodynamic quantities, and reaction barriers of uranyl hydrate (see refs 6c,d of the main paper). The use of hybrid functionals such as B3LYP, which is beneficial for many thermochemical applications,<sup>10</sup> is prohibitively expensive in conjunction with CPMD.

## 2. Details of Static Gas-Phase and PCM Computations

Geometries have been optimized with the Gaussian 03 program<sup>3</sup> in the gas phase at the BLYP/LANL2DZ(U)/SDD(Tc)/6-31G\*\* level, i.e. employing the Los Alamos relativistic ECP for U together with its (3s3p2d2f) valence basis of contracted Gaussians,<sup>11</sup> the Stuttgart-Dresden ECP for Tc,<sup>4</sup> standard 6-31G(d,p) basis for all other elements, and a medium-sized integration grid (75 radial shells with 302 angular points per shell). Optimized coordinates are appended below. Very similar energetics were obtained when the small-core Stuttgart-Dresden ECP together with a [7s6p5d3f] valence basis set was used for U<sup>12</sup> (where each of the most diffuse *s*-,*p*-,*d*-, and *f*-primitives have been omitted from the

original basis set, cf. the procedure adopted in reference 10), when relativistic all-electron calculations were performed employing the ZORA method (zeroth-order relativistic approximation) and a polarized triple-zeta basis of Slater functions as implemented in the ADF program package,<sup>13</sup> or when the BP86 functional was used (data not shown).

Single-point energy computations were performed for the gas-phase geometries at the same DFT level using a polarizable continuum<sup>14</sup> employing the parameters of water and UFF radii. For pristine nitrate and pertechnetate ions, the default settings in the Gaussian 03 program afford solvation energies of -61.6 kcal/mol and -55.4 kcal/mol, respectively, which can be compared to experimental estimates of the free energies of solvation, -71.7 kcal/mol and -58.6 kcal/mol, respectively.<sup>15</sup> Apparently, the stronger hydration of  $\text{NO}_3^-$  vs.  $\text{TcO}_4^-$  is somewhat underestimated with the simple PCM approach.



**Figure S1:** Electrostatic potential (BLYP/SDD(Tc)/6-31G\* level), color-coded from  $-0.25$  a.u. (red) to  $+0.25$  a.u. (blue) and mapped on an isodensity surface ( $\rho = 0.008$  a.u.); top: nitrate, bottom: pertechnetate.

The NPA<sup>16</sup> and ESP computations for nitrate and pertechnetate have been performed at the BLYP/SDD(Tc)/6-31G\* level detailed above. The approximate minima in the ESP values were located by inspecting the values on a suitable grid in space. The values reported in the main paper and plotted in Figure S1 were obtained in the gas phase for geometries fully optimized at that level, but very similar numbers are obtained with single-point PCM computations.

### Additional References

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### 3. Optimized Geometries

Cartesian coordinates, BLYP/LANL2DZ(U)/SDD(Tc)/6-31G\*\* optimized, together with total energies (E in a.u.) obtained at that level.

NO3- D3h (E = -280.31439)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.000000	0.000000	0.000000
2	8	0.000000	1.286547	0.000000
3	8	-1.114182	-0.643273	0.000000
4	8	1.114182	-0.643273	0.000000

TcO4- Td (E = -381.86261)

1	43	0.000000	0.000000	0.000000
2	8	1.013502	1.013502	1.013502
3	8	-1.013502	-1.013502	1.013502
4	8	-1.013502	1.013502	-1.013502
5	8	1.013502	-1.013502	-1.013502

H2O C2v (E = -76.39687)

1	8	0.000000	0.000000	0.121556
2	1	0.000000	0.763584	-0.486224
3	1	0.000000	-0.763584	-0.486224

[UO2(H2O)4(h1-NO3)]+ C1 (E = -787.88493)

1	92	-0.452726	0.013957	-0.055200
2	8	-1.980730	-1.975588	0.547107
3	8	3.767398	0.944785	0.535155
4	8	-0.086134	2.534755	-0.457417
5	8	1.775815	0.547926	-0.367503
6	8	-2.587181	1.148209	0.781686
7	8	-0.039563	-0.107534	1.706280
8	8	3.102487	-1.152683	0.251284
9	8	-1.207072	-0.006911	-1.707437
10	8	0.780393	-2.060883	-0.754947
11	7	2.962641	0.095925	0.185515
12	1	-1.777264	-2.476171	1.361926
13	1	-2.245380	-2.640269	-0.118521
14	1	0.870491	2.742115	-0.484681
15	1	-0.511338	3.069211	-1.155512
16	1	-2.758222	1.343875	1.723139
17	1	-3.438067	1.243339	0.312737
18	1	0.844674	-2.291188	-1.703084
19	1	1.724094	-1.923018	-0.429860

[UO2(H2O)3(h2-NO3)]+ C2v (E = -711.46674)

1	92	0.000000	0.000000	0.337401
2	8	0.000000	0.000000	-3.834008
3	8	0.000000	1.094329	-1.891383
4	8	-1.808083	0.000000	0.453413
5	8	0.000000	2.536057	0.604026
6	8	0.000000	-2.536057	0.604026
7	8	0.000000	-1.094329	-1.891383
8	8	1.808083	0.000000	0.453413
9	8	0.000000	0.000000	2.880475
10	7	0.000000	0.000000	-2.621048
11	1	-0.781228	3.062322	0.338715
12	1	0.781228	-3.062322	0.338715
13	1	-0.781228	-3.062322	0.338715
14	1	0.781228	3.062322	0.338715
15	1	0.785576	0.000000	3.461477
16	1	-0.785576	0.000000	3.461477

[UO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(h<sub>1</sub>-TcO<sub>4</sub>)]+ C1 (E = -889.38826)

1	92	1.199135	-0.061043	-0.032534
2	43	-2.706772	-0.083520	0.067349
3	8	0.996331	-0.197955	1.761039
4	8	1.767720	0.012391	-1.754390
5	8	2.059278	2.268814	0.691251
6	8	1.318769	-2.590939	-0.298606
7	8	3.674637	-0.451636	0.398858
8	8	-0.089189	2.078819	-0.924796
9	8	-0.971709	-0.653453	-0.235220
10	8	-3.116839	-0.301396	1.721457
11	8	-3.799968	-0.954435	-0.929311
12	8	-2.710150	1.617590	-0.335899
13	1	-1.064781	2.139185	-0.707976
14	1	-0.031625	2.161337	-1.898644
15	1	1.472750	2.915903	0.241737
16	1	2.059457	2.503971	1.640276
17	1	0.776054	-3.172982	0.269946
18	1	1.335880	-3.007831	-1.182801
19	1	4.119028	-0.573749	1.259676
20	1	4.372953	-0.380904	-0.280143

[UO<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(h<sub>2</sub>-TcO<sub>4</sub>)]+ C2v (E = -812.95607)

1	92	0.000000	0.000000	0.961759
2	8	0.000000	1.800176	1.112616
3	8	2.504478	0.000000	1.487243
4	8	-2.504478	0.000000	1.487243
5	8	0.000000	-1.800176	1.112616
6	8	0.000000	0.000000	3.493003
7	43	0.000000	0.000000	-2.334533
8	1	3.027790	0.780027	1.211359
9	1	-3.027790	-0.780027	1.211359
10	1	-3.027790	0.780027	1.211359
11	1	3.027790	-0.780027	1.211359
12	1	0.000000	-0.786865	4.071982
13	1	0.000000	0.786865	4.071982
14	8	1.323336	0.000000	-1.107864
15	8	-1.323336	0.000000	-1.107864
16	8	0.000000	1.411244	-3.306389
17	8	0.000000	-1.411244	-3.306389