

Supporting Information for

Structure of a uranyl peroxo complex in aqueous solution from first-principles molecular dynamics simulations.

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Additional Computational Details

CPMD simulations

The same methods and basis sets as in our previous studies of uranyl complexes¹ were employed. Car-Parrinello molecular dynamics (CPMD)² simulations were performed using the BLYP functional³ and norm-conserving pseudopotentials that had been generated according to the Troullier and Martins procedure⁴ and transformed into the Kleinman-Bylander form.⁵ For uranium, the semicore (or small-core) pseudopotential was employed that had been generated and validated in reference 6. Periodic boundary conditions were imposed using cubic supercells with a lattice constant of 13 Å. Kohn-Sham orbitals were expanded in plane waves at the Γ -point up to a kinetic energy cutoff of 80 Ry. Simulations were performed in the NVT ensemble using a single Nosé-Hoover thermostat set to 320 K (frequency 1800 cm⁻¹), a fictitious electronic mass of 600 a.u., and a time step of 0.121 fs. The boxes contained uranyl, one peroxo and one hydroxo ligand, and a total of 57 water molecules, affording a density of ca. 1.0. The system has one negative charge, neutralised by a uniform background charge. In order to maintain the time step, hydrogen was substituted with deuterium. Long-range electrostatic interactions were treated with the Ewald method. No electrostatic decoupling between replicated cells was included.

Constrained CPMD simulations were performed along a predefined reaction coordinate ξ (difference in bond distances Δr) connecting the different tautomeric complexes, in order to evaluate the change in the Helmholtz free energy by pointwise thermodynamic integration⁷ of the mean constraint force $\langle f \rangle$ along this coordinate via

$$\Delta A_{a \rightarrow b} = -\int_a^b \langle f(\xi) \rangle d\xi \quad (1).$$

At each point, the system was propagated until $\langle f(\xi) \rangle$ was sufficiently converged (usually within 1.5 - 2 ps after 0.5 ps of equilibration, similar to the degree of convergence documented in Figure S1 of the supporting information for reference 6. Each new point was continued from the final, equilibrated configuration of the previous one, using 3200 steps of continuous slow growth to decrease the constrained Δr . The point with largest $\langle f(\xi) \rangle$, at $\Delta r = 0.31$ Å, was retraced with a higher cutoff of 100 Ry and a timestep of 3 a.u. (for a total of 3 ps, restarted from the last point of the slow growth at 80 Ry after quenching to the Born-Oppenheimer surface). According to the root-mean-square displacement along the trajectories, the solutions remained liquid-like throughout.

Selected conformers were optimised in the gas phase until the maximum gradient was less than $5 \cdot 10^{-4}$ a.u. (denoted CP-opt).

QM/MM simulations:

We employed the CPMD/MM protocol previously validated,⁸ where the solute (a single complex **1a** or **2a**) is described at the same DFT level, whereas the solvent is described by the TIP3P model.⁹ The solvent consists of 3000 H₂O molecules in a periodic box of cell length 45.05 Å. Van-der-Waals parameters on OH⁻, H₂O, O₂²⁻ and OOH ligands were the same as in the TIP3P model.⁹ The systems were pre-equilibrated using the following sequence:

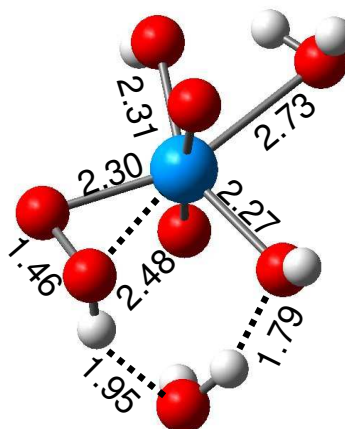
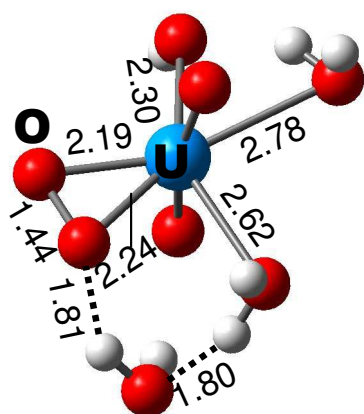
(i) *Classical pre-equilibration:* After 1000 steps of energy minimisation, 100 ps of MD were performed in the NVT ensemble (T = 320 K, starting from random velocities), followed by 100 ps of MD in the NPT ensemble (P = 1 atm, T = 320 K) and 500 ps of MD in the NVT ensemble (T = 320 K). These simulations were performed with the AMBER10 software.¹⁰ During the fully classical MD simulations, the solute was kept frozen (“belly” option in AMBER). Atomic charges on **1a** and **2a** were RESP charges computed at the B3LYP/6-31G** level and using a hyperbolic restraint of 0.001 a.u. (computed with the NWChem 6.1.1 software).¹¹ Atomic charges along with the corresponding cartesian coordinates are gathered below:

13		13	
XYZ coordinates of 1a + RESP charges (hyperbolic restraint 0.001 u.a.)		XYZ coordinates of 2a + RESP charges (hyperbolic restraint 0.001 u.a.)	
U 0.000360 -0.109678 -0.004974 2.2711		U 0.007416 0.023985 0.041886 2.4101	
O 0.420415 -0.229290 -1.774084 -0.7636		O -0.057091 0.294623 1.822235 -0.7196	
O -0.159829 0.306709 1.771761 -0.7855		O 0.009075 -0.189353 -1.760825 -0.7664	
O -2.193063 -0.216715 -0.343090 -0.4879		O 2.509185 0.148509 -0.180010 -0.4808	
O -1.667189 -1.517307 -0.020266 -0.5328		O 2.001400 -1.192941 0.151702 -0.5349	
O 1.964611 -1.203093 0.514618 -0.9441		O -1.331436 -1.879152 0.176594 -0.9180	
O 2.397315 1.277379 -0.265787 -0.8133		O -2.672118 0.297489 -0.144954 -0.7439	
O -1.263648 2.299932 0.026087 -0.7488		O -0.044555 2.219274 -0.258064 -0.9480	
H 2.093548 -1.395682 1.449362 0.3207		H -1.237199 -2.515087 -0.539989 0.2914	
H 2.419933 1.241774 -1.229313 0.3716		H -2.565726 -0.689701 -0.084925 0.3614	
H 2.639435 0.367036 0.046293 0.4021		H -2.810539 0.533570 -1.068094 0.3381	
H -2.060740 1.747836 -0.059309 0.3416		H -0.079572 2.792910 0.514311 0.3281	
H -1.114191 2.388472 0.976634 0.3689		H 2.695045 0.084063 -1.128228 0.3825	

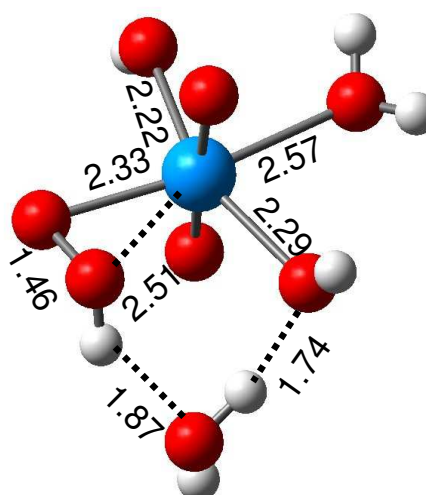
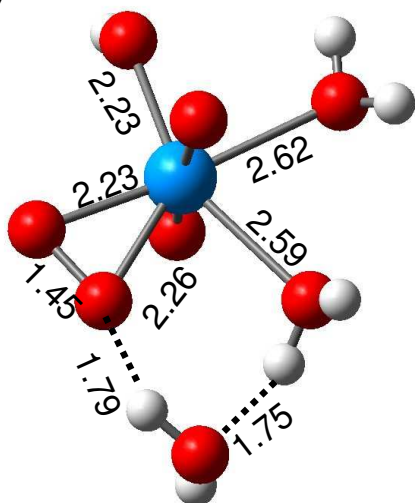
(ii) *DFT/MM pre-equilibration:* The last positions from the classical pre-equilibration step were taken and used as starting coordinates for an additional 3 ps of MD in the NVT ensemble (T = 320 K) starting from random velocities, using the CPMD/Gromos96 interface of CPMD.¹² The exact same simulation parameters as for full CPMD simulations were employed to describe the QM region. A non-periodic QM box of cell-length 15 Å was employed and the periodic images were decoupled using the Martyna-Tuckerman approach.¹³ The so-called “NN” and “ESP” domains were defined by a 16 Å and 36 Å cutoff, respectively. Typically, 200 and 1200 water molecules were included in the “NN” and “ESP” regions, respectively. Built-in values for the covalent radii ($r_{c,j}$) of MM atoms were used.¹² Wannier function centers (WFCs)¹⁴ were computed on the fly every 50 timesteps during production runs of 15 ps (NVT, at 320 K).

Full citations of the Gaussian suite of programs are provided in reference 15.

a) Gas phase



b) PCM



1a·H₂O

2a·H₂O

Figure S1: B3LYP/SDD optimised structures of **1a·H₂O** and **2a·H₂O** in a) the gas phase, and b) a continuum (PCM); selected distances are given in Å. Note the intramolecular H-bond between the water ligand trans to the peroxo moiety and the adjacent OH group that is present in the gas phase (top), but absent in solution (bottom).

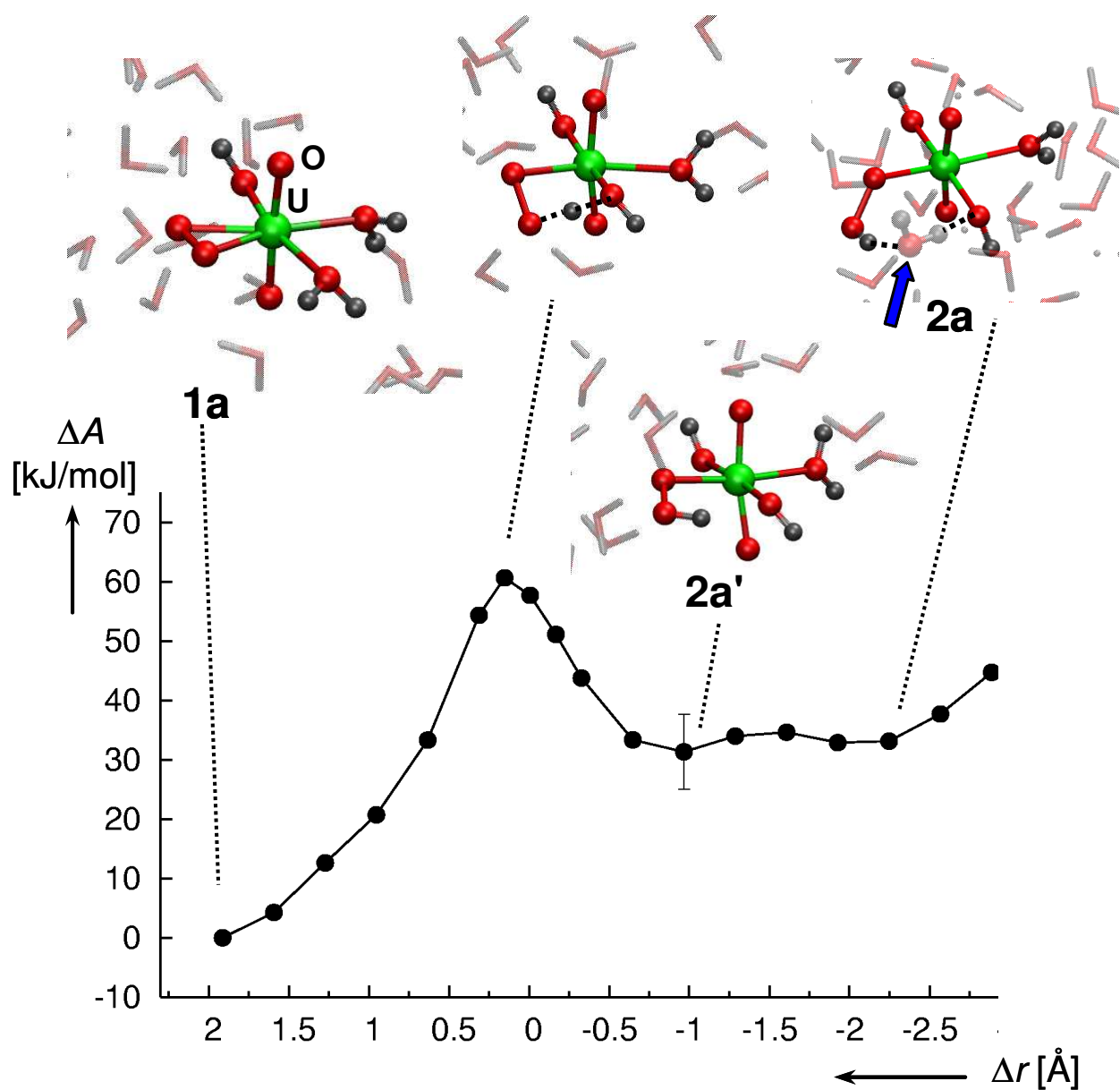


Figure S2: Magnified Figure 2 of the main paper. The water molecule from the solvent interacting with the OH groups from the complex in **2a** is highlighted with a blue arrow.

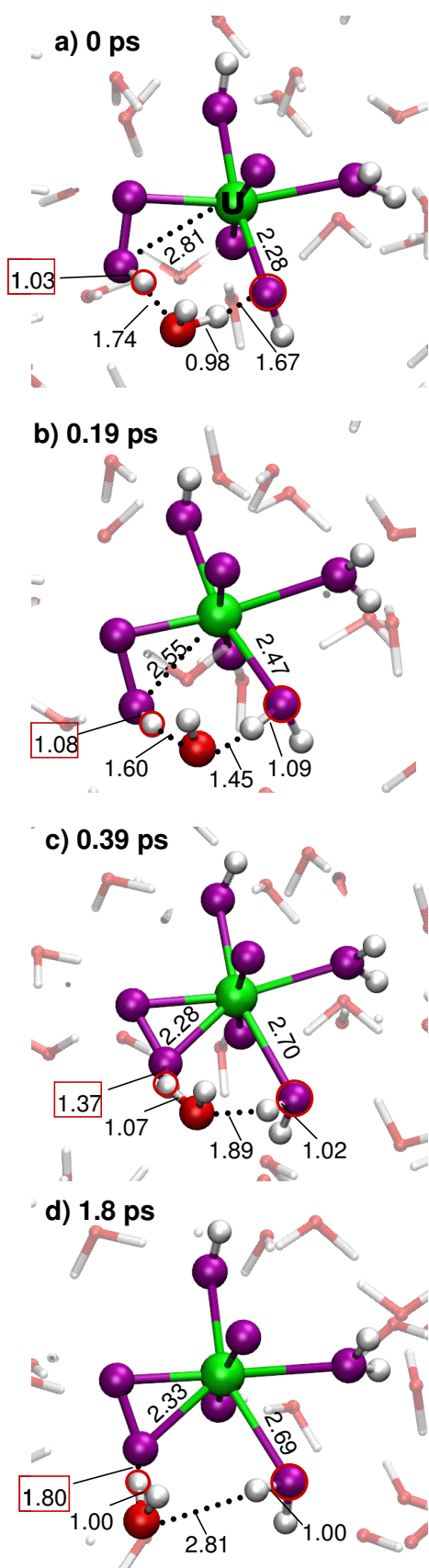


Figure S3: Spontaneous proton transfer during the constrained PTI step at $\Delta r = -1.61$ Å; the OH distance in the red box is included in the constraint, as well as the O...H distance between the atoms in red circles. Note how on going from the instantaneous snapshots a) to d) the solvent molecule (O atom shown in red) acts as relay for proton transfer from the OOH to the OH ligand. O atoms of the complex are shown in purple, selected distances are given in Å.

Table S1: Average (and standard deviation in parenthesis) of energy components from the PCM model;^a 50 single points from the constrained CPMD simulations.

Energy term	1a	2a
<i>Gas phase</i>		
SCF energies (in Hartree)	-1006.78611(864)	-1006.79774(870)
<i>In solution (PCM)</i>		
SCF energies (in Hartree)	-1006.95124(467)	-1006.93698(579)
Total free energy in solution (in Hartree) ^b	-1006.93351(461)	-1006.91853(571)
Polarized solute – solvent (kcal/mol)	-117.0(45)	-97.6(41)
Cavitation energy (kcal/mol)	21.9(26)	22.3(28)
Dispersion energy (kcal/mol)	-12.3(1)	-12.2(1)
Repulsion energy (kcal/mol)	1.5(1)	1.5(1)
Total non electrostatic (kcal/mol)	11.1(27)	11.6(28)

^aGaussian03 settings, BLYP/SDD/6-311+G** level; only the pristine complexes **1a** or **2a** were considered (the solvent has been removed at each step). ^bIncluding all non electrostatic terms.

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Cartesian coordinates of 1a and 2a and their water adducts

xyz format, B3LYP/SDD optimised

13
1a (gas)
U 0.000360 -0.109678 -0.004974
O 0.420415 -0.229290 -1.774084
O -0.159829 0.306709 1.771761
O -2.193063 -0.216715 -0.343090
O -1.667189 -1.517307 -0.020266
O 1.964611 -1.203093 0.514618
O 2.397315 1.277379 -0.265787
O -1.263648 2.299932 0.026087
H 2.093548 -1.395682 1.449362
H 2.419933 1.241774 -1.229313
H 2.639435 0.367036 0.046293
H -2.060740 1.747836 -0.059309
H -1.114191 2.388472 0.976634

13
1a (PCM)
U -0.055039 -0.080166 -0.002928
O 0.081577 0.030938 -1.831336
O 0.033100 -0.134718 1.829376
O -1.941196 1.128815 0.025400
O -2.271246 -0.290642 -0.047247
O 0.255799 -2.278482 -0.112856
O 2.561703 -0.135894 0.044094
O 0.890286 2.310501 0.079628
H 0.299259 -2.838658 0.682568
H 3.017984 0.435051 -0.601626
H 2.959328 -1.022723 -0.036186
H 0.678061 3.016685 -0.558207
H 1.228767 2.740784 0.886329

13
2a (gas)
U 0.007416 0.023985 0.041886
O -0.057091 0.294623 1.822235
O 0.009075 -0.189353 -1.760825
O 2.509185 0.148509 -0.180010
O 2.001400 -1.192941 0.151702
O -1.331436 -1.879152 0.176594
O -2.672118 0.297489 -0.144954
O -0.044555 2.219274 -0.258064
H -1.237199 -2.515087 -0.539989
H -2.565726 -0.689701 -0.084925
H -2.810539 0.533570 -1.068094
H -0.079572 2.792910 0.514311
H 2.695045 0.084063 -1.128228

13
2a (PCM)
U -0.029037 -0.031595 0.012076
O -0.037943 0.110359 1.832704
O -0.051033 -0.140455 -1.812651
O 2.374041 0.720369 -0.035044
O 2.212720 -0.737976 0.050696
O -0.591760 -2.167571 0.179441
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H -3.152447 -0.375074 -0.523698
H -2.825027 1.134648 -0.233852
H -0.402614 2.734029 0.638318
H 2.729693 0.871514 -0.942077

16
1a.H2O (gas)
U 0.212682 -0.132260 -0.028911
O 0.971540 -0.099886 -1.686394
O -0.447632 0.183138 1.650626
O -1.763871 -0.909062 -0.746803
O -0.923443 -1.984432 -0.281015
O 2.218538 -0.760364 0.910138
O 2.238508 1.758501 0.179479
O -1.297056 1.882367 -0.753606
H 2.211213 -0.967258 1.850442
H 2.480145 1.775131 -0.753610
H 2.620998 0.923012 0.551473
H -1.531208 1.660953 -1.662358
H -2.097622 1.693540 -0.204164
O -3.207792 0.736531 0.844270
H -2.947628 -0.070751 0.335826
H -2.613004 0.698960 1.608661

16
1a.H2O (PCM)
U 0.283843 -0.102929 -0.021054
O 0.803350 -0.085707 -1.775044
O -0.167450 0.086871 1.737937
O -1.655402 -1.161820 -0.512908
O -0.639192 -2.130762 -0.132486
O 2.291032 -0.891963 0.546894
O 1.594001 2.151922 0.234392
O -1.404863 1.802248 -0.475518
H 2.530950 -1.039084 1.468981
H 1.507097 2.857073 -0.418615
H 2.538066 2.045357 0.405504
H -1.530605 2.124632 -1.375636
H -2.288833 1.515966 -0.140293
O -3.572869 0.454192 0.418119
H -3.017444 -0.354018 0.324092
H -3.841613 0.519683 1.341882

16
2a.H2O (gas)
U 0.198374 -0.076391 -0.025640
O 0.887089 -0.339881 -1.676824
O -0.405517 0.335810 1.632862
O -1.950381 -1.055262 -0.775348
O -1.109920 -1.962890 0.003486
O 2.111489 -0.942172 0.927112
O 2.442346 1.475983 0.062848
O -0.941002 1.769667 -0.718203
H 2.095885 -1.112954 1.874255
H 2.750081 0.617997 0.453115
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H -2.594487 -0.666150 -0.143769
O -3.163087 1.012658 0.677525
H -2.701711 0.914270 1.520859
H -2.499666 1.480163 0.110376

16
2a.H2O (PCM)
U -0.260868 -0.074004 0.017825
O -0.725718 -0.347789 1.754204
O 0.168003 0.274827 -1.711572
O 1.925930 -1.132184 0.636072
O -1.026947 -2.015263 -0.109982
O -2.085691 -1.177041 -0.607003
O -2.021594 1.791836 -0.114954
O 1.011570 1.757531 0.536420
H -2.304969 -1.305031 -1.537390
H -2.945834 1.523004 -0.049567
H -1.918712 2.607926 0.389242
H 1.105336 2.021101 1.459293
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O 3.375069 0.875716 -0.437318
H 3.520297 1.138420 -1.353271
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