

Supporting Information for

Effect of Counterions on Structure and Stability of Aqueous Uranyl(VI) Complexes. A First-Principles Molecular Dynamics Study.

Michael Bühl, Georg Schreckenbach, Nicolas Sieffert, and Georges Wipff

Computational Details

The same methods and basis sets as in our previous studies of uranyl fluorides¹ 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 somewhat higher temperature was chosen to increase solvent mobility and improve the sampling. These unconstrained simulations were followed over several picoseconds (up to 4 ps), the last 2 ps of which were taken for collection of the data presented in Table 1 of the main paper.⁷ The boxes contained 57 extra water molecules, minus the number of NH₄⁺ ions, affording a density of ca. 1.0. 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, as it had been shown that no noticeable errors are introduced by this procedure for divalent ions,⁸ and no artifacts were apparent even for trivalent ones.⁹ Starting structures were generated from previous well-equilibrated simulations from reference 1 by manually changing ligands or replacing water molecules with the appropriate number of ammonium ions.

Constrained CPMD simulations were performed along predefined reaction coordinates (bond distances r) connecting complexes with different coordination numbers, in order to evaluate the change in the Helmholtz free energy by pointwise thermodynamic integration¹⁰ of the mean constraint force $\langle f \rangle$ along these coordinates via

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

At each point, the system was propagated until $\langle f \rangle$ 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 2000 steps of continuous slow growth to increase the constrained distance. Uncertainties were estimated from the largest standard deviation of the running average of $\langle f \rangle$ during the last ps of the constrained runs, multiplied with the total integration width.¹¹

All computations were performed with the CPMD program.¹² Because the simulations were performed at constant volume, Helmholtz rather than Gibbs free energies are obtained, but in condensed phase the difference between both should be very small. No further dissection of the free energies into enthalpic and entropic contributions (which would require, in principle, simulations at different temperatures) was attempted.

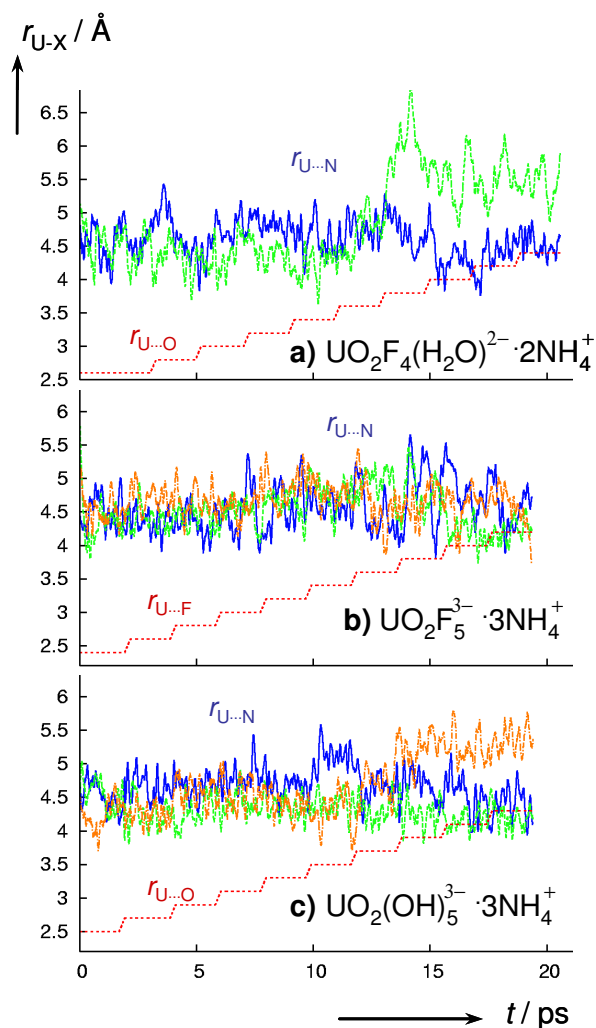


Figure S1: Mobility of the ammonium ions during the constrained CPMD simulations, monitored via the U...N distances (blue, green, and orange lines) along the reaction paths depicted in Figures 1 and 2 of the main paper. Note the large fluctuations and the onset of diffusion, visible in the green curve in part a) and the orange curve in part c), where distances exceeding 5-6 Å in the last third of the paths denote passage of the NH_4^+ from the first into the second solvation shell. Red dotted lines are the constrained distances illustrating the progress of the dissociation under scrutiny.

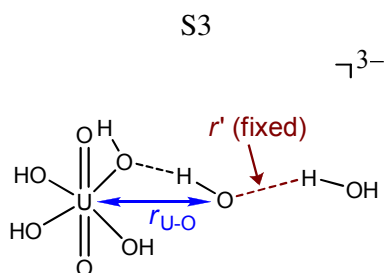


Figure S2: Illustration of additional constraint r' during OH^- dissociation from **3** in water (including counterions), using the labeled $r_{\text{U-O}}$ distance as reaction coordinate.

References

- (1) Bühl, M.; Sieffert, N.; Wipff, G. *Chem. Phys. Lett.* **2009**, *467*, 287-293.
- (2) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471-2474.
- (3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
- (4) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993-2006.
- (5) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425-1428.
- (6) Bühl, M.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2005**, *127*, 13506-13507.
- (7) It is difficult to ensure full equilibration after such a short time. In some cases the simulations may just be metastable, and much longer simulation times might be needed to reach the true ground states. However, all observable parameters discussed, i.e. bond distances or mean constraint forces, were reasonably well converged within the duration of the simulations, without showing noticeable drifts.
- (8) Marx, D.; Hutter, J.; Parrinello, M. *Chem. Phys. Lett.* **1995**, *241*, 457-462.
- (9) Bühl, M.; Grigoleit, S.; Kabrede, H.; Mausnick, F. T. *Chem. Eur. J.* **2006**, *12*, 477-488.
- (10) Sprik, M.; Ciccotti, G. *J. Chem. Phys.* **1998**, *109*, 7737-7744, and references cited therein.
- (11) This uncertainty refers to the numerical precision of the PTI technique. The absolute uncertainty due to the accuracy of the underlying quantum-chemical methodology (density functional, pseudopotential, basis set) is, arguably, considerably higher, and is at least ± 2.5 kcal/mol, judged from the errors in computed kinetic and thermodynamic parameters relative to experiment (see reference 2 in the main paper).
- (12) CPMD Version 3.13.1, Copyright IBM Corp. 1990-2008, Copyright MPI für Festkörperforschung Stuttgart 1997 - 2001.