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

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Inclusion of NH_4^+ as counterions in Car-Parrinello molecular dynamics (CPMD) simulations of anionic uranyl(VI) complexes is proposed as viable approach to model "real" aqueous solutions. For $[UO_2F_4(H_2O)]^{2-}$ in water, it is shown that inclusion of two NH_4^+ ions strengthens the bond between uranyl and the water ligand by ca. 2 kcal/mol, improving the accord with experiment. According to CPMD simulations for $[UO_2X_5][NH_4]_3$ in water (X = F, OH), the fifth fluoride is bound much stronger than the fifth OH^-. Implications for a recently proposed model for oxygen exchange in uranyl hydroxide are discussed.

In order to make the vision of a virtual actinide lab come true, reliable computational modeling of actual experimental conditions is of the essence. Classical molecular dynamics (MD) simulations are an attractive way to account for conditions involving temperature, solvents, and counterions.[1] Combining this know-how with the accuracy achievable with current flavors of density functional theory (DFT) by way of DFT-based MD techniques has opened new and fruitful routes to study actinide complexes in silico.[2,3] We have been using the Car-Parrinello MD (CPMD) approach to model structural, kinetic, and thermodynamic properties of a variety of uranyl(VI) complexes in aqueous solution. For the simple uranyl hydrate, aqueous $[UO_2(H_2O)_5]^{2+}$, a protocol involving constrained CPMD/BLYP simulations and pointwise thermodynamic integration (PTI) has been successfully applied to compute free energies of deprotonation[2c] and the barrier for water exchange,[2b] as well as the binding energies of nitrate,[2d] chloride,[2e] and fluoride[2f] ligands. In all these cases, experimental reference data have been reproduced within ca. ±2.5 kcal/mol, a respectable accuracy for present-day DFT. The more involved dynamical approach often outperforms static computations with simple continuum models for solvation.

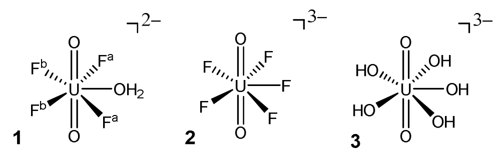

Chart 1.

During our studies of uranyl fluorides, $[UO_2F_4(H_2O)]^{2-}$ (**1**, Chart 1) has emerged as daunting challenge for theory because at all levels applied, the water ligand turned out to be unbound.[2f] Even though a shallow minimum appears for this ion in CPMD/PTI simulations, a free energy for water dissociation of ΔA = −7.2 kcal/mol was obtained. This result appeared to be at odds with experiment, because this ion has been characterized by X-ray crystallography[4] and because there is evidence for its existence in aqueous solution from EXAFS data.[5] Static optimizations and CPMD simulations have reproduced the stability of this ion in the crystal environment of $[UO_2F_4(H_2O)][NMe_4]_2{\cdot}2H_2O$, and have shown that the presence of the counterions is instrumental for this stability.[6] Because the EXAFS experiments have employed a large (9-fold) excess of NaF in order to produce the tetrafluoride, it has been speculated that this excess of counterions in solution, which was not included in the CPMD simulations, could help to stabilize the water ligand.[2f] We now report the first CPMD simulations addressing this question by taking counterions explicitly into account.[7]

Rather than using Na^+, a large and sluggish ion due to its rigid hydration sphere, we first explored smaller "onium" ions for this purpose. Hydronium ions, H_3O^+, were deemed highly attractive because of their fast proton transport in water and, hence, an expected fast equilibration. However, initial efforts to simulate an aqueous solution of $[UO_2F_4(H_2O)][H_3O]_2$ were thwarted by rapid protonation of a fluoride ligand and concomitant HF dissociation from the uranyl center. No such problems were encountered with ammonium ions, and simulations of $[UO_2F_4(H_2O)][NH_4]_2$ with fixed U-O(water) distances remained stable for a total of ca. 20 ps along the water dissociation pathway. Initially placed close to the fluoride ligands in the first solvation shell (see first snapshot in Figure 1), the ammonium ions tumbled noticeably and showed also some diffusive mobility, see Figure S1 in the Supporting Information (SI).

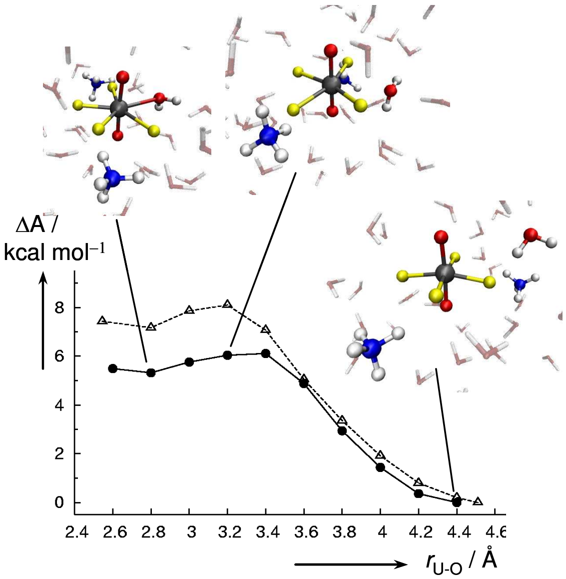

Figure 1. Change in free energy, ΔA, upon dissociation of the water ligand from **1** at 320 K. Triangles and dashed line: pristine ion in water, from reference 2f; circles and solid line: with two NH_4^+ counterions, showing selected typical snapshots from the trajectories. Reaction coordinates are the U-O distances.

Table 1: Computed and experimental geometrical parameters (distances in Å) for aqueous uranyl fluoride and hydroxide complexes. Mean values (in parentheses: standard deviations) over 2 ps of CPMD trajectories are reported, both for pristine ions and with *n* NH_4^+ gegenions present (*n* is the negative charge of the complex).

Complex/parameter	pristine	+ *n* NH_4^+	X-Ray[a]	EXAFS[a]
$[UO_2F_4(OH_2)]^{2-}$ (**1**)				
d(U=O)	1.86(3)[b]	1.86(3)[b]	1.79[c]	1.80[d]
d(U-O)	2.83(5)[b]	2.75(18)[b]	2.47[c]	2.48[d]
d(U-F[a])	2.30(9)[b]	2.29(9)[b]	2.26[c]	2.26[d]
d(U-F[b])	2.25(8)[b]	2.27(8)[b]	2.29[c]	2.26[d]
$[UO_2F_4]^{2-}$				
d(U=O)	1.86(2)[e]	1.87(4)	-	-
d(U-F)	2.24(7)[e]	2.24(7)	-	-
$[UO_2F_5]^{3-}$ (**2**)				
d(U=O)	1.87(4)	1.86(4)	1.76±0.03[f]	1.80[d]
d(U-F)	2.33(7)	2.34(8)	2.24±0.02[f]	2.26[d]
$[UO_2(OH)_4]^{2-}$				
d(U=O)	1.89(4)[g]	1.91(3)[g]	1.82(1)[h]	1.83(0)[i]
d(U-O)	2.30(6)[g]	2.29(7)[g]	2.26(2)[h]	2.26(5)[i]
$[UO_2(OH)_5]^{3-}$ (**3**)				
d(U=O)	-[j]	1.88(4)	-	1.79(1)[h]
d(U-O)	-[j]	2.43(9)	-	2.22(1)[h]

[a] Including estimated uncertainties, where available. [b] During ca. 1 ps of metastable simulation before water dissociation, see text. [c] Reference 4a. [d] Reference 5. [e] From reference 2f. [f] Reference 9. [g] Simulation containing an additional OH^- in the bulk. [h] Reference 13. [i] Reference 12. [j] Unstable (spontaneous OH^- protonation and dissociation of resulting water ligand).

The water-dissociation profile with counterions (solid line in Figure 1) is qualitatively similar to that without (dashed line), showing the same shallow minimum at $r_{U\text{-}O} \approx$ 2.8 Å. However, the driving force for water dissociation is noticeably reduced upon NH_4^+ addition, from −7.2 kcal/mol to −5.3 kcal/mol. Recalling that hybrid functionals[8] are likely to further reduce this value (by ca. 2 kcal/mol according to B3LYP single-point calculations),[2f] the simulations are now more consistent with a noticeable population of **1** in solutions of high ionic strength. When the constraint is lifted at the end of the run with $r_{U\text{-}O}$ = 2.6 Å, the water ligand stays bound for ca. 1.3 ps, fluctuating around *r* = 2.75 Å (Table 1), before finally trailing off into the bulk. The same had been found for pristine **1** in water, where a slightly larger mean distance of *r* = 2.83 Å had been obtained,[2f] consistent with the reinforcement of the uranyl-water bond upon addition of the counterions. Quantitatively, the uranyl-water affinity in aqueous **1** suggested by EXAFS (refined *r* = 2.48 Å),[5] is still underestimated considerably. Nonetheless, inclusion of NH_4^+ appears to be a viable way to model effects of counterions computationally.

This approach has been further explored for $[UO_2F_5]^{3-}$ (**2**), which is known in the solid state.[9] In order to probe for the possible existence of **2** in aqueous solution, we have run unconstrained CPMD simulations without and with three NH_4^+ ions present in the box. In both simulations, the complex remains stable for up to 4 ps. Subsequently, we have followed the dissociation of one F^- in the system with the counterions. After passing a barrier of $\Delta A^\ddagger$ = 6.7 kcal/mol, the free energy appears to level off at ΔA = 4.4±1.1 kcal/mol (filled circles in Figure 2), marking the formation of an outer-sphere complex. Adding a simple correction from the literature for full dissociation of an ion pair composed of a di- and a monoanion, $\Delta\Delta G$ = −2.4 kcal/mol,[10] affords a final estimate of ΔA = −2.0 kcal/mol for the reverse reaction, i.e. fluoride binding to the tetrafluoride:

$$[UO_2F_4]^{2-} + F^- \rightarrow [UO_2F_5]^{3-} \quad (1)$$

Interestingly, a noticeable driving force is predicted for this process. Experimentally, this value is unknown, but from the free fluoride-binding energies of uranyl di- and trifluoride, ΔG^o = −3.2 kcal/mol and −1.1 kcal/mol,[11] respectively, a small and positive value can be inferred for ΔG of eq 1. The simulated ΔA value of −2.0 kcal/mol is thus probably just within the usual error margin of our CPMD-based approach for uranyl complexes, ±2.5 kcal/mol,[2b-f] suggesting that with counterions, even highly charged ions can be described reasonably well with our methodology.

Finally, we have studied a related complex that has attracted renewed interest, $[UO_2(OH)_5]^{3-}$ (**3**). Identified by EXAFS as possible[12] or even major component[13] in highly alkaline uranyl solutions, this ion has recently been proposed as an intermediate involved in the oxygen scrambling between axial oxo and equatorial O-donor ligands.[14] In an unconstrained CPMD run in pure water, pristine **3** is found to be unstable: it immediately deprotonates a neighboring water molecule, affording $[UO_2(OH)_4(H_2O)]^{2-}$. The latter, much like the related fluoride **1**, quickly loses the coordinated water ligand under formation of $[UO_2(OH)_4]^{2-}$. When an unconstrained simulation is started from **3** surrounded by three NH_4^+ ions near the equatorial plane, one of the latter ions is deprotonated to give $[UO_2(OH)_4(H_2O)]^{2-}$ and NH_3. Apparently, **3** is much more basic than **2**. To avoid this problem, we fixed all NH distances in the simulations of [**3**][NH_4]$_3$ to the mean value over the unconstrained run for [UO_2F_4][NH_4]$_2$, 1.05 Å. With this setup, [**3**][NH_4]$_3$ remained (meta-)stable for 3 ps.

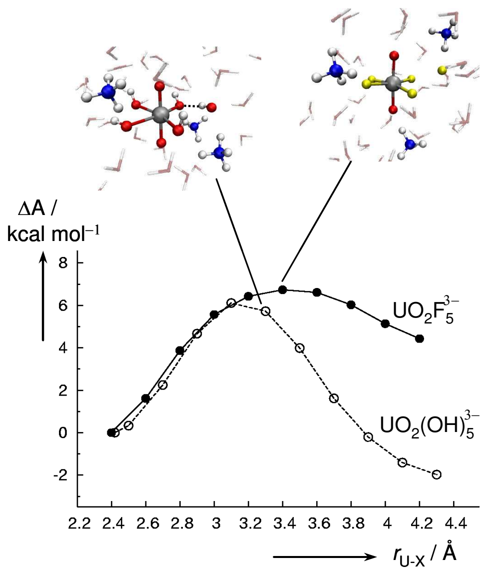

Figure 2. Changes in free energy, Δ*A*, upon dissociation of one of the equatorial ligands from **2** (solid line and circles) and **3** (dashed line and open circles) including counterions at 320 K. Selected snapshots are shown near the transition state regions.

Eventually, the distance between U and the O atom of an OH^- ligand flanked by two NH_4^+ ions was taken as reaction coordinate and was elongated stepwise to afford the profile displayed in Figure 2 (open circles). At r = 2.7 Å, the dissociating OH^- abstracted a proton from a nearby water molecule, initiating the well-known relay mechanism for proton transport in water.[15] To keep the simple distance coordinate, from that point onwards the (U)HO···HOH hydrogen bond was frozen at 1.57 Å, the mean value before proton transfer (see Figure S2 in the SI). No other proton abstractions were encountered on the rest of the path.

Up to r = 3.1 Å, the dissociation profile is very similar to that of **2**, but beyond that distance the forming $[UO_2(OH)_4]^{2-}\cdot OH^-$ ion pair is stabilized significantly. Inspection of the trajectories reveals one possible reason for this finding: at that point the dissociating OH^- "turns back" to the uranyl complex, donating a hydrogen bond to a neighboring hydroxide ligand (see dotted line in the top left snapshot in Figure 2). As a dissociating F^- cannot do this, the resulting $[UO_2F_4]^{2-}\cdot F^-$ ion pair is much higher in energy. For the hydroxide, after passing a barrier of $\Delta A^\ddagger$ = 6.1 kcal/mol, the outer-sphere complex is reached at ΔA = –2.0±1.1 kcal/mol. With the same correction for full dissociation mentioned above, a driving force of ΔA = 4.4 kcal/mol is obtained for the reverse process, eq 2, with a corresponding barrier of $\Delta A^\ddagger$ = 10.5 kcal/mol.

$$[UO_2(OH)_4]^{2-} + OH^- \rightarrow [UO_2(OH)_5]^{3-} \qquad (2)$$

This process has recently been suggested to be the rate-limiting step in the exchange between O atoms from the uranyl moiety and equatorial ligands.[14] Static DFT/PBE computations with a polarizable continuum model of solvation have afforded $\Delta G^\ddagger$ = 21.3 kcal/mol ($\Delta H^\ddagger$ = 12.5 kcal/mol),[14] in apparent qualitative accord with experiment, $\Delta G^\ddagger$ = 15.2 kcal/mol at 298K ($\Delta H^\ddagger$ = 9.8 kcal/mol).[13] Our estimated free activation energy, 10.5 kcal/mol, is smaller, but is in the same ballpark as these data, inviting further investigation of this intriguing exchange process.

In summary, we propose to use NH_4^+ as simple model counterion in CPMD simulations of anionic uranyl complexes. For $[UO_2F_4(H_2O)]^{2-}$, addition of two such counterions strengthens the bond between the metal and the water ligand noticeably, by ca. 2 kcal/mol, thereby improving the accord with respect to experiment. Applying this methodology to pentacoordinate $[UO_2X_5]^{3-}$ species reveals interesting intrinsic differences between X = F, which is predicted to be bound, and X = OH, which is predicted to be unbound. By mimicking actual experimental conditions, an ever more realistic and accurate modeling of uranyl chemistry in solution is within reach.

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Supporting Information Available: Computational details and further graphical material. This material is available free of charge on the Internet at http://pubs.acs.org.

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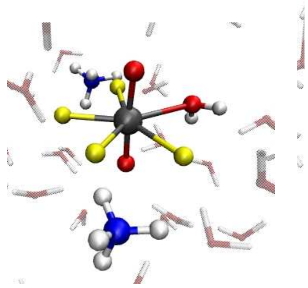
Graphical abstract



NH_4^+ ions are proposed as model counterions in Car-Parrinello molecular dynamics simulations of anionic uranyl(VI) complexes in water, such as $[UO_2F_4(H_2O)]^{2-}$ (see adjacent graphic) or $[UO_2X_5]^{3-}$ (X = F, OH).