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Mechanism of Water Exchange in Aqueous Uranyl(VI) Ion. A Density Functional Molecular Dynamics Study

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Constrained Car–Parrinello molecular dynamics simulations and thermodynamic integration have been performed for an associative pathway of water exchange between aqueous $[UO_2(OH_2)_5]^{2+}$ and bulk water. The simulated free energy of activation for this process, 6.7 kcal mol^{-1}, is significantly lower than that computed for a purely dissociative mechanism, 10.8 kcal mol^{-1}. Because the transient hexahydrate is indicated to have no chemically significant lifetime, the exchange mechanism can be classified as associative interchange.

How do ligand-exchange reactions proceed at transition-metal centers? Rates of such processes can be measured with a variety of techniques, but elucidation of the underlying mechanisms is far more difficult.[1] Quantum-chemical calculations can complement experimental studies by identifying the most favorable pathways for ligand-substitution reactions.[1c] The reliability of such computations hinges on the proper treatment of electron-correlation and solvation effects. The latter are of particular importance for ions in polar, protic solvents, for example, in the prototypical water-exchange reactions between ligands from the first and second solvation shells in aquo complexes.

We have recently become interested in the coordination number of the metal center in uranyl(VI) hydrate and other uranyl(VI) complexes.[2] According to Car−Parrinello molecular dynamics (CPMD)[3] simulations with a pointwise thermodynamic integration (PTI) scheme, dissociation of one water molecule from aqueous $[UO_2(OH_2)_5]^{2+}$, affording aqueous $[UO_2(OH_2)_4]^{2+}$, is endergonic on the Helmholtz free-energy surface by $\Delta A = 8.7$ kcal mol^{-1}. The free-energy barrier of $\Delta A^{\ddagger} = 10.8$ kcal mol^{-1} for this process was found to be comparable with the free energy of activation for water exchange between $[UO_2(OH_2)_5]^{2+}$ and the bulk, $\Delta G^{\ddagger} = 9.1$ kcal mol^{-1} at 298 K, as derived by ^{17}O NMR spectroscopy.[4] It was noted, however, that "no definite conclusion can be drawn from this result regarding the mechanism for this process, dissociative vs associative or interchange".[2a] We now present a constrained CPMD study of the latter pathways, allowing such a conclusive prediction.

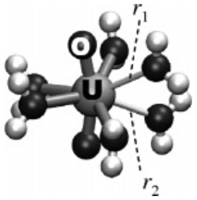

Figure 1. Starting structure for simulations of transient, six-coordinate $[UO_2(OH_2)_6]^{2+}$ (corresponding to, e.g., structure III in ref 15f).

We employed the same methods and parameters[5] as those in our study of the dissociative mechanism.[2a] To model the putative six-coordinate, transient $[UO_2(OH_2)_6]^{2+}$, we immersed a corresponding structure in a periodic water box, constraining two adjacent U−O(H$_2$) bonds to be equal (labeled r_1 and r_2 in Figure 1). When propagated for a total of 3.3 ps, this constrained structure remained stable, with mean constrained distances of $r_1 = r_2 = 2.69(12)$ Å [in parentheses is the standard deviation; the mean value for the four unconstrained U−O(H$_2$) bonds is 2.51(10) Å]. The mean constraint force $\langle f \rangle$ remained close to zero (4×10^{-4} au), suggesting that this form could be either an intermediate or a transition state. When the constraint was lifted after 3.3 ps

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[1] For recent reviews, see for instance: (a) Helm, L.; Merbach, A. E. *Chem. Rev.* **2005**, *105*, 1923. (b) Richens, D. T. *Chem. Rev.* **2005**, *105*, 1961. (c) Rotzinger, F. P. *Chem. Rev.* **2005**, *105*, 2003.

[2] (a) Bühl, M.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2005**, *127*, 13506. (b) Bühl, M.; Kabrede, H.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.*, in press.

[3] Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

[4] Calculated from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values given in: Farkas, I.; Bányai, I.; Szabó, Z.; Wahlgren, U.; Grenthe, I. *Inorg. Chem.* **2000**, *39*, 799.

[5] CPMD simulations were performed with the CPMD program (CPMD version 3.7.0; copyright by IBM Corp. and Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany), the gradient-corrected BLYP functional (Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098; Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785), and norm-conserving Troullier−Martins pseudopotentials (Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993; Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425); see the Supporting Information of ref 2a for further details concerning construction and validation of the semicore pseudopotential for *U*. Periodic boundary conditions and a cubic cell (lattice constant 13.0 Å) that contained UO_2^{2+} and a total of 59 water molecules (not 66, as was erroneously stated in ref 2a) were used, yielding a density of 1.0. Kohn−Sham orbitals were expanded in plane waves up to a kinetic energy cutoff of 80 Ry. Molecular dynamics simulations were performed in the NVT ensemble using a single Nosé−Hoover thermostat set to 300 K, a fictitious electronic mass of 600 au, and a time step of 0.121 fs. To maintain this time step, *H* was substituted with *D*. Optimizations were performed in the gas phase until the maximum gradient was less than 5×10^{-4} au.

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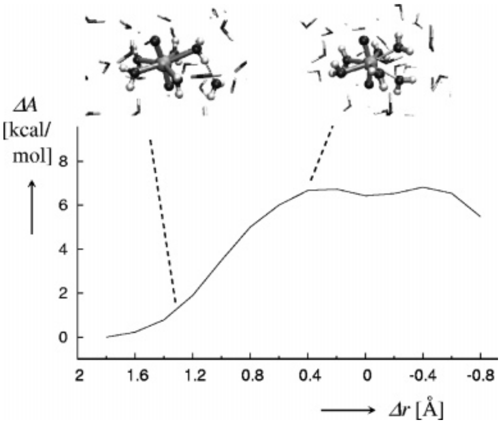

Figure 2. Change in free energy, ΔA, for associative displacement of one water ligand from $[UO_2(OH_2)_5]^{2+}$ with one from the second hydration sphere, as obtained from thermodynamic integration (reaction coordinate: difference $\Delta r = r_1 - r_2$, as defined in Figure 1). Top: representative snapshots from early and late stages of association.

and the system was propagated freely, one of the constrained water molecules was immediately expelled from the complex into the bulk, with the corresponding $U \cdots O(H_2)$ distance increasing steadily and exceeding 3.5 Å after 0.3 ps. This result thus strongly argues against a genuine, associative *A* mechanism and makes an interchange pathway more likely.

To study such a path more quantitatively with the PTI technique,[6] we constructed a reaction coordinate by fixing the difference $\xi = \Delta r = r_1 - r_2$ at successively larger values (in step sizes of 0.2 Å) and propagating the system at each point until $\langle f(\xi) \rangle$ was sufficiently converged.[7] Helmholtz free energies[8] were then evaluated according to

$$\Delta A_{a \to b} = -\int_a^b \langle f(\xi) \rangle \, d\xi \tag{1}$$

via numerical integration. With increasing distance r_1, the leaving water molecule gradually accepts a hydrogen bond from the other aquo ligand included in the constraint. At $\Delta r = 1.8$ Å, $\langle f(\xi) \rangle$ is again close to zero, because the distant water molecule is now incorporated in the second solvation sphere, i.e., well within a region where the $U-O(H_2)$ pair correlation function of the unconstrained pentahydrate in water has its second, broad maximum.[2b] Taking this point as the reference state with $\Delta A = 0$, the free-energy profile depicted in Figure 2 is obtained.

Relative to this five-coordinate reference state, the six-coordinate form with $\Delta r = 0$ is higher in free energy by 6.4 kcal mol^{-1}. Of the different coordination modes studied so far, five-coordination is thus clearly preferred in water.[9] The highest point on the free-energy surface in Figure 2 is found for $\Delta r = 0.2$ Å, corresponding to a barrier of $\Delta A^{\ddagger} = 6.7$ kcal mol^{-1} for the interchange path. This value is noticeably lower than the experimental free-energy barrier, 9.1 kcal mol^{-1}, but consistent with the tendency of present-day density functionals (DFTs) to underestimate, rather than overestimate, reaction barriers.[10] More importantly, the barrier computed for this interchange mechanism is significantly lower, by more than 4 kcal mol^{-1}, than that for dissociation, ruling out the latter as the predominant water-exchange pathway.

Interchange pathways can further be classified into I_a, I, or I_d mechanisms, depending on the relative advancement of bond breaking vs bond formation in the transition state, as reflected in the activation volume.[1,11] We use Rotzinger's bond-length criterion as an indicator for the latter:[1c,12] On going from the five-coordinate state at $\Delta r = 1.8$ Å to the transition-state region at $\Delta r = 0$ or 0.2 Å, the sum of all six $U-O(H_2)$ distances (mean values along the designated trajectories) decreases significantly, from 16.4 to 15.4 Å. Thus, the reaction coordinate sampled by our CPMD simulations is consistent with an I_a pathway.

When the reaction coordinate in Figure 2 is extended to $\Delta r = -0.8$ Å, i.e., toward the final product with exchanged water molecules, a slight increase in the free energy is found, followed by a steep drop, essentially mirroring the points between $\Delta r = 0$ and 0.8 Å. According to these results, the symmetric six-coordinate form with $\Delta r = 0$ might be characterized as a shallow minimum. Its rapid decay in an unconstrained molecular dynamics (MD) run, however, (see above) argues against the presence of such an intermediate with a chemically significant lifetime, and the whole region between $\Delta r = -0.4$ and $+0.4$ Å is probably best described as a shallow, rugged plateau. A representative snapshot from this area is included in Figure 2.

To assess the role of the solvent, which turned out to be of paramount importance for the *D* path,[2a] we attempted to drive pristine $[UO_2(OH_2)_6]^{2+}$ in the gas phase (again starting from a structure like that shown in Figure 1) along the same reaction coordinate Δr toward a $[UO_2(OH_2)_5]^{2+} \cdot H_2O$ adduct. These attempts were thwarted, however, by the occurrence of spontaneous rearrangement to four-coordinate $[UO_2(OH_2)_4]^{2+} \cdot 2H_2O$ at some point along this path (irrespective from which side the path was followed, i.e., forward from the six-coordinate or backward from a 5 + 1 form). Apparently, the thermodynamic stability of the (hydrated) four-coordinate species over the five-coordinate one in the gas phase ($\Delta A = -2.2$ kcal mol^{-1} for $5 \rightarrow 4 + 1$[2a]) provides a

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(6) See for instance: Sprik, M.; Ciccotti, G. *J. Chem. Phys.* **1998**, *109*, 7737 and references cited therein.

(7) Usually within 2−3 ps after 0.5 ps of equilibration, similar to the degree of convergence documented in Figure S1 of the Supporting Information for ref 2a. The largest standard deviation for the running average of $\langle f(\xi) \rangle$ over the final picosecond of any point was ca. 5×10^{-4} au; multiplied with the total integration width of 1.8 Å, this corresponds to an estimated numerical uncertainty of ca. 1 kcal mol^{-1} for the derived energies. Each new point was started from the final, equilibrated configuration of the previous one.

(8) NVT simulations yield ΔA; because the actual volume change at constant pressure is very small, ΔA and ΔG should be very similar.

(9) U−O bond distances in solution can be determined fairly well with X-ray-based methods such as EXAFS, but the coordination number is more difficult to refine. For aqueous uranyl, between ca. 4.5 and 6 equatorial water ligands have been inferred (for a recent review, see: Den Auwer, C.; Simoni, E.; Conradson, G.; Madic, C. *Eur. J. Inorg. Chem.* **2003**, 3843). For a recent X-ray scattering study favoring a hydration number slightly smaller than 5, see: Neuefeind, J.; Soderholm, L.; Skanthakumar, S. *J. Phys. Chem. A* **2004**, *108*, 2733.

(10) For instance, see: (a) Andzelm, J.; Baker, J.; Scheiner, A.; Wrinn, M. *Int. J. Quantum Chem.* **1995**, *56*, 733. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2001.

(11) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479.

(12) Rotzinger, F. P. *J. Am. Chem. Soc.* **1997**, *119*, 5230.

sink on the free-energy surface that prevents construction of a simple reaction coordinate connecting five- and six-coordinate forms. As a rough guide for the energetic preferences in the gas phase, we computed relative energies on the potential energy surface by optimizing a number of isomeric, pristine $[UO_2(OH_2)_5]^{2+}\cdot H_2O$, $[UO_2(OH_2)_6]^{2+}$, and $[UO_2(OH_2)_4]^{2+}\cdot 2H_2O$ structures with the same setup as that used in the CPMD simulations.[5] For the lowest minima found in each case (see the Supporting Information), relative energies of $\Delta E = 0$, $+10.8$, and -2.5 kcal mol^{-1}, respectively, are obtained. Consistent with the MD results, four-coordination is clearly preferred in the gas phase (whereas it is strongly disfavored in solution[2a]). Six-coordinate species are quite high in energy both in the gas phase and, judging from the free energies, in water as well.

Besides possible inherent shortcomings of the accuracy of the particular flavor of density function theory (DFT) employed,[13] the precision of our ΔA values may further be limited by a potentially incomplete sampling due to the short simulation times[7] that are presently possible. The choice of an improper reaction coordinate might also introduce a spurious bias; our difference coordinate, arguably, is flexible enough to adapt itself to a variety of associative and dissociative pathways and to let the system find the most favorable one. However, when another PTI path was started from a well-equilibrated unconstrained CPMD simulation of aqueous $[UO_2(OH_2)_5]^{2+}$, pulling in one water molecule from the second solvation sphere via the same Δr coordinate used so far (i.e., by modeling the reverse reaction of that used for generating the data of Figure 2), a gradual accumulation of excess mean forces was observed on going from $\Delta r = 2$ to 0.4 Å, at which point both water molecules involved in the constraint spontaneously drifted off into the bulk, leaving four-coordinate $[UO_2(OH_2)_4]^{2+}$ behind.[14] Up to this point, the computed free energy had risen to 10.4 kcal mol^{-1}, in very good accord with the barrier for the dissociative process using a single bond length as the reaction coordinate ($\Delta A^{\ddagger} = 10.8$ kcal mol^{-1}).[2a] There is thus no guarantee that a particular reaction coordinate produces a unique pathway. In principle, however, the computed relative free energies between the initial and final states should be independent of the path between them, and it is unlikely that our simulated free-energy difference between five- and six-coordinate forms, around 6−7 kcal mol^{-1}, is plagued by an artifact of our PTI procedure. As far as this barrier is concerned, our computational protocol passes the ultimate test against experiment reasonably well, at least qualitatively, and we are confident that the I_a pathway as emerging from our simulations is a faithful representation of the actual water-exchange mechanism.

The mechanism of this exchange process[15] has previously been studied by Vallet et al.,[16] who optimized salient minima and transition states at the Hartree−Fock (HF) level, followed by MP2 single-point energy calculations, all including a continuum solvation model (CPCM). The *D* mechanism was highly unfavorable throughout, and the activation energies for the *A* pathway were computed as 5.0 and 4.5 kcal mol^{-1} at HF and MP2 levels, respectively. These levels were recently criticized as being inadequate because of the lack or insufficient treatment of electron correlation.[1c,17] In a recent MD study of aqueous uranyl(VI) involving an ab initio (CASPT2)-derived force field,[18] singular events described as associative or "something between *A* and *I*" were observed.

In conclusion, we have presented the first quantum-chemical study of the solvent exchange at aqueous uranyl(VI) hydrate that takes the effects of solvation and dynamics explicitly into account. This approach goes beyond the common practice of performing static optimizations including solvation only implicitly via continuum models and furnishes unprecedented insights into the mechanistic details of this exchange process. The free-energy barrier simulated for an associative interchange pathway agrees qualitatively with experiment and is significantly lower than that for a pure *D* mechanism. Within the limitations of present-day density functionals concerning their quantitative accuracy, CPMD simulations can now be used to study structure, speciation, and substitution reactions of uranyl species in an aqueous solution.

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Supporting Information Available: Cartesian coordinates for optimized $[UO_2(OH_2)_5]^{2+}\cdot H_2O$, $[UO_2(OH_2)_6]^{2+}$, and $[UO_2(OH_2)_4]^{2+}\cdot 2H_2O$ structures. This material is available free of charge on the Internet at http://pubs.acs.org.

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(13) For many hydrates of the first transition row, present-day density functionals (including BLYP) are indicated to underestimate the stability of higher coordination numbers. See: Rotzinger, F. R. *J. Phys. Chem. B.* **2005**, *109*, 1510. In some cases, hybrid functionals such as B3LYP may be more accurate than "pure" functionals such as BLYP; unfortunately, the use of hybrid functionals in CPMD is prohibitively expensive. In conjunction with the semicore pseudopotential, the BLYP functional has proven quite robust in reproducing geometries and energies from experiment or ab initio or other DFT computations (see ref 2 and this work). See also: Schreckenbach, G.; Hay, P. J.; Martin, R. L. *J. Comput. Chem.* **1999**, *20*, 70.

(14) The main difference between the two pathways is that in the one starting from the six-coordinate form, one bond between uranyl and a water ligand trans to the two constrained ones is significantly weakened, as is apparent from the mean U−O(H$_2$) distances between 2.63(13) and 2.52(11) Å for that bond along the total trajectory. For the reverse path starting from the five-coordinate species, the four unconstrained U−O(H$_2$) bonds remain approximately equivalent.

(15) For other quantum-mechanical studies concentrating on the coordination number of the uranyl unit, see, for example: (a) Spencer, S.; Gagliardi, L.; Handy, N. C.; Ioannou, A. G.; Skylaris, C. K.; Willets, A.; Simper, A. M. *J. Phys. Chem. A* **1999**, *103*, 1831. (b) Hay, J. P.; Martin, R. L.; Schreckenbach, G. H. *J. Phys. Chem. A* **2000**, *104*, 6259. (c) Tsushima, S.; Suzuki, A. *J. Mol. Struct. (THEOCHEM)* **2000**, *529*, 21. (d) Clavaguéra-Sarrio, C.; Brenner, V.; Hoyau, S.; Marsden, C. J.; Millié, P.; Dognon, J.-P. *J. Phys. Chem. B* **2003**, *107*, 3051. (e) Moskaleva, L. V.; Krüger, S.; Sporl, A.; Rösch, N. *Inorg. Chem.* **2004**, *43*, 4080. (f) Cao, Z.; Balasubramanian, K. *J. Chem. Phys.* **2005**, *123*, 114309. (g) Shamov, G. A.; Schreckenbach, G. *J. Phys. Chem. A* **2005**, *109*, 10961−10974.

(16) Vallet, V.; Wahlgren, U.; Schimmelpfennig, B.; Szabo, Z.; Grenthe, I. *J. Am. Chem. Soc.* **2001**, *123*, 11999.

(17) See, however: Vallet, V.; Macak, P.; Wahlgren, U.; Grenthe, I. *Theor. Chem. Acct.* **2006**, *115*, 145−160.

(18) Hagberg, D.; Karlström, G.; Roos, B. O.; Gagliardi, L. *J. Am. Chem. Soc.* **2005**, *127*, 14250.