Communication

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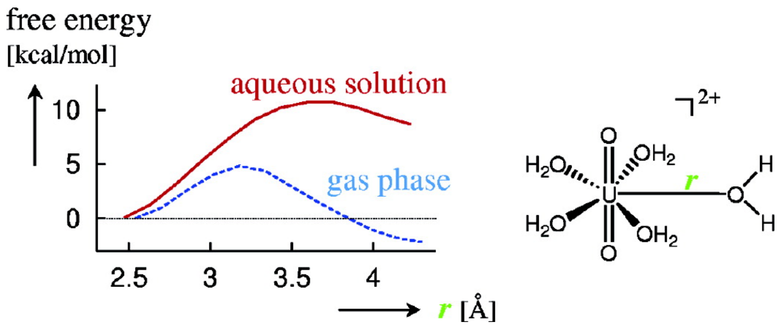
J. Am. Chem. Soc., **2005**, 127 (39), 13506-13507• DOI: 10.1021/ja054186j • Publication Date (Web): 13 September 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Coordination Environment of Aqueous Uranyl(VI) Ion

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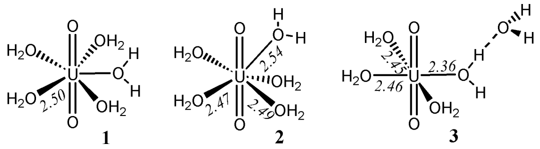
The solution chemistry of the uranyl(VI) ion, UO_2^{2+}, is central to the reprocessing of nuclear waste. This process usually involves dissolution of the spent nuclear fuel in aqueous nitric acid and extraction of recyclable uranium in the form of uranyl complexes with suitable scavenger molecules.[1] Better control of these processes requires detailed insights into structure and dynamics of the key species involved in the relevant elementary steps. Classical molecular dynamics (MD) simulations of uranyl complexes have significantly contributed to our understanding of these factors at an atomic level,[2] simulations that are being guided and augmented by an increasing number of quantum-mechanical (QM) studies.[3]

Among the possible species present in aqueous mixtures, the simple hydrated uranyl ion, $[UO_2(OH_2)_n]^{2+}$, has received considerable attention. According to recent X-ray scattering experiments,[4] there is a dynamic equilibrium between five-coordinated uranyl ($n = 5$), which is ubiquitous in single crystals with a plethora of counterions, and a four-coordinated form ($n = 4$), which has not been observed so far. QM studies at appropriate levels of ab initio or density functional theory (DFT) agree that five-coordination is more favorable and that a surrounding polar solvent can have a large impact on the relative energies of the various species.[3a,e] To date, essentially all of these studies taking solvation effects into account did so by using static geometries with solvated clusters and/or a simple polarizable continuum model (PCM) or one of its variants. We now go beyond these simple static approaches and present state-of-the-art Car−Parrinello molecular dynamics (CPMD)[5] simulations of the aqueous solution as a dynamic ensemble, treating solute and solvent on equal footing.[6] Such simulations have been shown to hold great promise for the description of structure, dynamics, and properties of aqueous solutions of transition-metal complexes.[7] We now call special attention to structure and dynamics of the aqueous uranyl(VI) ion and to relative stabilities of four- and five-coordinated forms.

Geometry optimizations and CPMD simulations were performed with the CPMD program,[8] the gradient-corrected BLYP functional,[9] and norm-conserving Troullier−Martins pseudopotentials[10] (for details concerning construction and validation of the pseudopotential for U, see Supporting Information). Periodic boundary conditions and a cubic cell (lattice constant 13.0 Å) were used that contained UO_2^{2+} and a total of 5 or 66 water molecules for the gas phase and aqueous solution, respectively. Kohn−Sham orbitals were expanded in plane waves up to a kinetic energy cutoff of 80 Ry. MD 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, hydrogen was substituted with deuterium (for further details, see Supporting Information).

Initial optimizations and MD simulations were performed for gaseous $[UO_2(OH_2)_5]^{2+}$. Starting from several five-coordinate configurations with different orientations of the H atoms, the optimizations converged to essentially two distinct stationary points on the potential energy surface (PES), one with approximate D_5 (**1**) and one with approximate C_s symmetry (**2**); see Scheme 1. Structure **1** with planar UOH_2 moieties and with the H atoms essentially aligned along the UO_2 axis is the commonly observed minimum. Structure **2** has a distinctly nonplanar, envelope-like arrangement of the equatorial O atoms about U. Both forms **1** and **2** are similar in energy and are 3.9 and 3.5 kcal/mol, respectively, above an isomeric tetracoordinate water adduct, $[UO_2(OH_2)_4]^{2+}\cdot H_2O$ (**3**).

Scheme 1. Optimized $[UO_2(OH_2)_5]^{2+}$ Isomers (*in italics:* selected bond distances in Å)



In a CPMD simulation in the gas phase, **1** and **2** rapidly interconvert into each other [mean U−O(H_2) distance 2.54(8) Å], and no spontaneous dissociation affording **3** is observed. To assess the relative stability of five- and four-coordinated species further, we performed constrained MD simulations along a predefined reaction coordinate connecting both forms and evaluated the change in the Helmholtz free energy by pointwise thermodynamic integration (PTI)[11] of the mean constraint force $\langle f\rangle$ via

$$\Delta A_{a\rightarrow b} = -\int_a^b \langle f(r)\rangle \mathrm{d}r$$

We chose one U−O(H_2) distance r as the reaction coordinate and increased its value successively from 2.54 Å in steps of 0.16 Å. 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). The resulting free energy profile in the gas phase is shown in Figure 1 (dashed line).

In terms of ΔA, the product, **3**, is more stable than the reactant by 2.2 kcal/mol in the gas phase, consistent with the above-mentioned relative energies on the PES, in particular, when allowing for entropy effects. Starting from **1**, the free energy barrier is reached at 4.8 kcal/mol.

When $[UO_2(OH_2)_5]^{2+}$ is placed in a water box, the mean U−O(H_2) distance during 4.5 ps, 2.47(9) Å, is shorter than that in the gas phase and is in good accord with previous calculations (e.g., 2.50 Å at BLYP/PCM)[3a] and with distances observed in the solid or in solution (e.g., 2.42 Å from X-ray scattering).[4] No spontaneous water dissociation from **1** occurred during the simulations in water. Likewise, no water molecule was captured within ca. 6 ps from the solvent during a CPMD simulation of aqueous, four-coordinated $[UO_2(OH_2)_4]^{2+}$.

When the PTI procedure is repeated for aqueous $[UO_2(OH_2)_5]^{2+}$, a reaction profile notably different from that in the gas phase is

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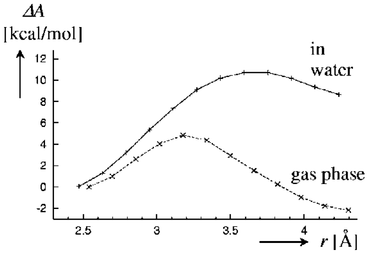

Figure 1. Change in free energy, ΔA, for dissociation of one water ligand from $[UO_2(OH_2)_5]^{2+}$, as obtained from thermodynamic integration (reaction coordinate: U−O distance *r*).

obtained. Starting from the five-coordinated form, a barrier of 10.8 kcal/mol is reached at $r = 3.75$ Å, and the final $[UO_2(OH_2)_4]^{2+}$ state is found 8.7 kcal/mol above the reactant. The latter value is similar to a previous static BLYP/PCM estimate (7.2 kcal/mol).[3a] The barrier can be compared to an MP2/PCM estimate of 17.7 kcal/mol for this dissociative process, based on a static, optimized transition state with a breaking U−O bond of 3.98 Å.[12] Incidentally, our CPMD-derived barrier is in good accord with the free energy of activation for water exchange between $[UO_2(OH_2)_5]^{2+}$ and the bulk, 9.1 kcal/mol at 298 K, as derived by ^{17}O NMR spectroscopy.[13] No definite conclusion can be drawn from this result regarding the mechanism for this process, dissociative versus associative or interchange. The latter paths, which are favored by MP2/PCM calculations,[12] should also be followed with constrained MD simulations.

It should be noted at this point that the simulated free energies in Figure 1 are subject to numerical uncertainty due to potentially incomplete sampling. In addition, the choice of a simple bond distance as reaction coordinate can introduce a spurious bias that may affect the final ΔA values.[14] We are confident, however, that these errors and uncertainties will not exceed a few kcal/mol. For instance, the largest standard deviation of the running average of $\langle f \rangle$ from the final value encountered for all points, multiplied by the total integration width, amounts to 1.5 kcal/mol.

Arguably, the largest uncertainty arises from the particular quantum-chemical method employed, BLYP in our case. Due to the lack of accurate thermochemical measurements, it is difficult to assess the inherent accuracy of a given theoretical level. For example, for the simple water detachment in the gas-phase

$$[UO_2(OH_2)_5]^{2+} \rightarrow [UO_2(OH_2)_4]^{2+} + H_2O$$

dissociation energies between 23.5 kcal/mol (BLYP/DZP)[3a] and 29.8 kcal/mol (MP2)[13] have been reported. Our BLYP value, 20.6 kcal/mol,[15] is somewhat lower than the literature data, but is reasonably close to related DFT results. The important point is, however, that even if four-coordination as in **3** would be preferred in the gas phase, solvation would reverse this order. Thus, our results emphasize the important role of the solvent environment on the nature and structure of the first solvation shell of the uranyl ion and strongly support a clear predominance of five-coordinate $[UO_2(OH_2)_5]^{2+}$ over four-coordinate $[UO_2(OH_2)_4]^{2+}$ in water.

In summary, we have presented the first pure quantum-chemical MD study of aqueous uranyl(VI) ion. These simulations have furnished insights into the picosecond dynamics of the well-known $[UO_2(OH_2)_5]^{2+}$ ion and on the energetics for water dissociation from it. Most significantly, DFT-based MD simulations of realistic uranyl complexes in solution are now possible that can serve as a bridge between static QM calculations and classical MD studies. Simulations of the type presented here can be important ingredients in the toolbox of computational chemists who strive to understand the dynamic processes in nuclear waste extraction and, ultimately, to devise better ways for controlling them.

Acknowledgment. M.B. wishes to thank W. Thiel and the MPI für Kohlenforschung for support, H. M. Senn and S. Thiel for helpful discussions, the Rechenzentrum Garching for a generous allotment of CPU time on an IBM p690 “Regatta” cluster, and I. Weidl for on-site technical support.

Supporting Information Available: Details concerning construction and validation of the pseudopotential for uranium and optimized coordinates of **1**−**3**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(15) Note that this value is inherently free of basis set superposition error.

JA054186J