Hydration and Water-Exchange Mechanism of the UO_2^{2+} Ion Revisited: The Validity of the "$n + 1$" Model

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Hydration and water-exchange mechanism of the UO_2^{2+} ion was studied by the B3LYP calculations. Relative Gibbs energies in aqueous phase of the 4-, 5-, and 6-fold uranyl(VI) hydrates were compared. A model with a complete first hydration shell and one water in the second shell was used (which is called "$n + 1$" model) to compare the energy of the UO_2^{2+} ion with different hydration numbers. The $n + 1$ model tends to overestimate the overall stability of the complex, and this type of model should be carefully used for the determination of the coordination number or the coordination mode such as unidentate or bidentate. A stable 5-fold uranyl(VI) hydrate goes through a very rapid water-exchange process via an associative (*A*-) mechanism keeping the 5-fold uranyl(VI) the dominant species.

1. Introduction

In several previous publications,[1−14] it has been shown that the quantum chemical calculations and quantum chemically derived potential calculations (molecular dynamics (MD) and Monte Carlo (MC) simulations) can be used to estimate the hydration number of actinyl (V, VI) ions and also their water-exchange mechanisms. In former type of calculations, the actinyl (V, VI) ion with a saturated first hydration shell is treated quantum chemically, and the rest of the solvation sphere is modeled by polarizable continuum model (PCM), conductor-like polarizable continuum model (CPCM), or conductor-like screening model (COSMO). To compare the Gibbs energy of the complex having different hydration numbers, one water was put in the second shell (like $AnO_2(H_2O)_n(H_2O)^{2+/+}$) for the model with a smaller hydration number. The model with a larger hydration number has all water molecules in the first shell (like $AnO_2(H_2O)_{n+1}{}^{2+/+}$). In the present article, I call the former type of model as "$n + 1$" model. Generally, the $n + 1$ model is preferred above adding the aqueous Gibbs energy of two independent complexes "n" ($AnO_2(H_2O)_n{}^{2+/+}$) and "1" (H_2O). The reason is that there is a double counting of solvation sphere if one simply adds the energy of n and 1 models, while this is not the case for the $n + 1$ model. Various types of computational methods have been tested on the UO_2^{2+} hydrate including HF, MP2, CCSD, BLYP, B3LYP, and CAS-SCF. The major conclusion on the uranyl(VI) hydration is that the hydration number of the UO_2^{2+} ion is 5 and is independent of computational method or basis sets as far as proper sizes of effective core potential (ECP) and basis sets are used. The difference in the hydration energy mostly depends on the geometry differences. The result also critically depends on the choice of the solvation model and the radius; this point has been focused and well studied by Gutowski and Dixon in their recent article.[13] Very recently, Rotzinger claimed that the MP2 calculation is inappropriate for studying the uranyl(VI) hydration because "inappropriate treatment of electron correlation can lead to incorrect conclusions".[14] However, Vallet et al. pointed out that what Rotzinger claims as "improper treatment of electron correlation" is merely a result of using different geometries in comparing two different theories, and Rotzinger's claim that the MP2 is inappropriate for the calculation of the water-exchange reaction of the uranyl(VI) ion is wrong and is not supported by any scientific data.[15]

In this article, the hydration and the water-exchange reaction of the uranyl(VI) ion is studied at the B3LYP level by following the same procedure as previous works, but the potential energy surface (PES) was searched more carefully. The validity of using the $n + 1$ type model combined with the CPCM solvation energy will be the focus.

2. Computational Method

All computational models were tried with several tens of different initial structures to ensure that the optimized structure is the real global minimum of the potential energy surface (PES). Geometry optimizations were performed in the aqueous phase at the B3LYP level. Calculations at the B3PW91 level in solvent and at the MP2 level in gas phase were also tested in some computational models. Aqueous-phase calculations were performed through the use of CPCM[16] (conductor-like polarizable continuum model) using UAHF radii (united atom topological model applied on radii optimized for the HF level of theory)[17] as implemented in Gaussian 03 package of programs.[18] Small-core effective core potentials (ECPs) were used on uranium, neptunium, and oxygen with corresponding basis sets.[19] The most diffuse basis functions on uranium and neptunium with the exponent 0.005 were omitted, and a d-function on oxygen basis was included. For hydrogen, a 5s contracted to 3s basis set[20] was used, adding a diffuse p-function in the MP2 calculations. In the MP2 calculations, correlation energy was calculated without correlating 5s, 5p, and 5d electrons of uranium. All calculations were performed using Gaussian 03 program. Precursors, intermediates, and transition states were confirmed to be the real states through vibrational frequency analyses with no or single imaginary frequency present. Transition states were only searched at the B3LYP level. Gibbs energy was calculated as in previous work[4] but with using the parameters $p = 1$ atm and $T = 298.15$ K. All energies refer to the Gibbs energy in aqueous phase unless it is specifically described.

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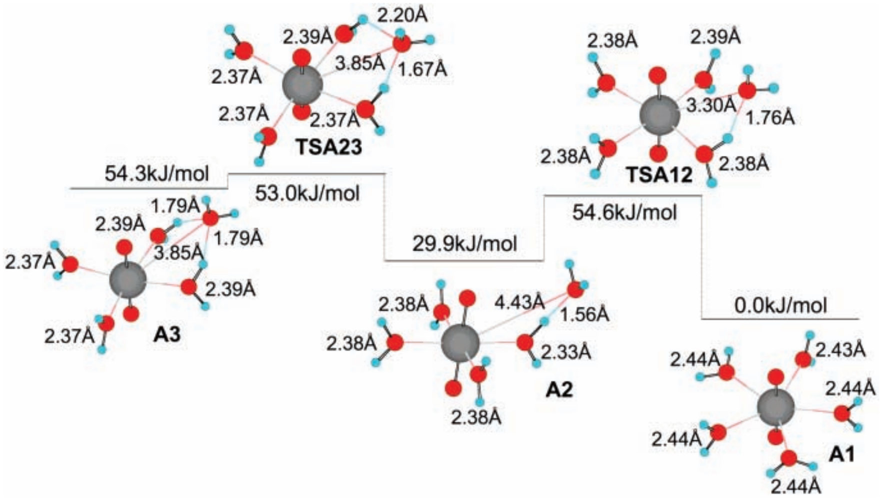

Figure 1. The optimized structures and the Gibbs energies in the aqueous phase of the 4-fold and the 5-fold uranyl(VI) hydrates and the transition states between them. The Gibbs energy value is relative to the complex A1.

3. Results and Discussions

The structure of the $UO_2(H_2O)_5{}^{2+}$ ion was optimized at the B3LYP level in the aqueous phase, and it was found that the structure having two planar waters plus three perpendicular waters toward the equatorial plane is the most stable geometry (Figure 1 A1). This is the same structure as obtained by Rotzinger[14] at the CAS-SCF(12/11)-PCM level calculation (Figure 2b in ref 14). It is also similar to the structure obtained by Bühl et al. using Car−Parrinello MD,[11] but they obtained the structure with single planar plus four perpendicular waters in the first hydration sphere. The difference between the present result and the results by Bühl et al. might be associated with the fact that the calculations by Bühl et al. were made in the gas phase.[21] However, the conformation of waters may depend on computational parameters such as exchange−correlation (XC) functional, solvation model, and solute radii, thus, this result should not be considered to be very conclusive.

The "4 + 1" models (four waters in the first shell and one water in the second shell) have also been tested, and A2 and A3 were obtained as the stable intermediates. The transition states between A1 and A2 and between A2 and A3 have also been identified (Figure 1). The 4-fold uranyl(VI) (A2) was found to lie 29.9 kJ/mol above the 5-fold uranyl(VI) (A1), and its activation Gibbs energy was found to be 54.6 kJ/mol. This result is in good agreement with the result obtained by Vallet et al.[5] except that Vallet et al. did not try A2 model in their study. The present result is also essentially in agreement with the MC results obtained by Clavaguéra-Sarrio et al.[6] as far as the gas-phase energy is concerned. The gas-phase energy difference between the "5" (A1) and the 4 + 1 (A3) models in the present calculation is 6.8 kJ/mol, but the 4 + 1 is more stable. It is not appropriate to use the gas-phase energy to discuss the stable hydration number. The surrounding solvent and the entropy play crucial roles to the total binding energy.

The Gibbs energy difference between two 4 + 1 models, A2 and A3, is 24.4 kJ/mol and is surprisingly large. Contrary to this, the gas-phase energy difference between A2 and A3 is only 0.3 kJ/mol. The large Gibbs energy difference between A2 and A3 comes from the entropy term (ST) and also from the solvation energy. The solvation energy of the complexes A2 and A3 is 875.0 and 888.1 kJ/mol, respectively, and the aqueous entropy of A2 and A3 is 545.6 and 572.8 J/mol·K, respectively. These two factors make A2 to be much more stable than A3. There is a problem with the A2 model, however, that the $H_I \cdots O_{II}$ bond distance between the first and the second shell waters is 1.561 Å and is much shorter than a normal hydrogen bond distance. The $U-O_{II}$ distance of 4.427 Å in A2 is also much shorter than the experimentally obtained $U-O_{II}$ distance of 4.50 Å by Soderholm et al.[22] using high-energy X-ray scattering (HEXS). The density functional theory (DFT) calculation is known to overestimate the hydrogen bond strength and thereby tends to underestimate the hydrogen bond distance. Siboulet et al. optimized the structure of $UO_2{}^{2+}$ with complete first and second hydration shells at the B3LYP level and obtained the $H_I \cdots O_{II}$ bond distance of 1.70 and 1.79 Å for $UO_2(H_2O)_4(H_2O)_8{}^{2+}$ and $UO_2(H_2O)_5(H_2O)_{10}{}^{2+}$, respectively.[23] Similarly, Gutowski and Dixon also optimized the structures of $UO_2(H_2O)_4(H_2O)_8{}^{2+}$ and $UO_2(H_2O)_5(H_2O)_{10}{}^{2+}$ at the B3LYP level and obtained the $H_I \cdots O_{II}$ bond distance of 1.67 and 1.64−1.97 Å, respectively.[13] Therefore, it is not a DFT problem that is encountered here, but the problem is due to a strong electrostatic attraction of "+1" water by the $UO_2{}^{2+}$ cation using an "ill-shaped" model which lacks the rest of the second hydration sphere. The problem with the A2 model is that a short $H_I \cdots O_{II}$ bond distance can overestimate the stability of the 4 + 1 complex by decreasing the cavity of the solute and thereby increasing the absolute solvation energy of the solute. The CPCM solvation energy of the two different structures of $UO_2(H_2O)_4(H_2O)^{2+}$ were compared with one having an optimized $U-O_{II}$ distance of 4.427 Å and the other having an experimental $U-O_{II}$ distance of 4.50 Å.[22] The CPCM energy difference between the two geometries is 0.3 kJ/mol, the former having larger solvation energy. Similarly, the entropy of the two complexes was compared and the difference was found to be 2.7 J/mol·K, which corresponds to 0.8 kJ/mol at 298 K. Therefore, although the *n* + 1 model gives inaccurate geometry, the loss in accuracy of energy from the model is only about 1 kJ/mol. Geometry optimizations of the "5" and the 4 + 1 models were also tried at the B3PW91 and the MP2 levels, essentially giving the same hydrogen bond distances (see Supporting Information). The $H_I \cdots O_{II}$ bond distance in the A2-type 4 + 1 complex is 1.543 Å at the B3PW91 level in the aqueous phase and 1.512 Å at the MP2 level in the gas phase.

There is also a problem in the A3 model that this cannot be the symmetric point of the water-exchange reaction unless there is another water molecule that also has two hydrogen bonds to the first-shell waters. Such a complex consequently has a very low number of waters in the second hydration shell, and there

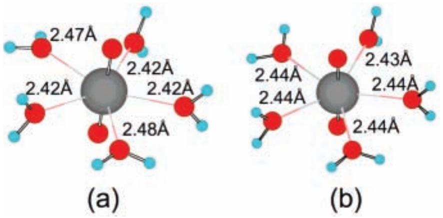

Figure 2. The optimized structure of the 5-fold uranyl(VI) hydrate in the aqueous phase corresponding to the electronic energy minimum (a, left). The complex on the right-hand side (b) has the Gibbs energy 6.4 kJ/mol lower than the complex on the left-hand side (a).

will be a significant difference with the second hydration sphere of $UO_2(H_2O)_5^{2+}$ where each water in the first shell binds two waters in the second shell.[24] With such a large structural difference, the kinetic process of water-exchange reaction would be very slow. This is not in line with what was experimentally found by Ikeda et al. that the water-exchange reaction in the UO_2^{2+} ion is rather rapid.[25] It was also not possible to identify the transition state between the A1 and the A3, and it always goes through the intermediate A2. Therefore, A2 is a more reasonable model as an intermediate of the dissociative (*D*-) water-exchange pathway, but a short $H_I \cdots O_{II}$ bond distance makes its energy to be less precise. One way to overcome this problem is to include a complete second hydration shell as Shamov and Schreckenbach,[9] Gutowski and Dixon,[13] and Siboulet et al.[23] did in their work. However, to search a global minimum of such a large molecule having relatively flat PES is very complicated and therefore was not tried in the present study. Such a large molecule potentially has a large number of local minima and might need to be investigated by MD or MC simulations. Searching a Gibbs energy minimum of much smaller $UO_2(H_2O)_5^{2+}$ ion is not at all easy because current computational scheme searches the PES of the electronic energy and not that of the Gibbs energy. Structure optimizations in this study were tried with several tens of different initial structures, but this does not yet guarantee that the real global minimum has been identified. The difficulty is that the electronic energy minimum is not necessary the Gibbs energy minimum. It was found that Figure 2a is the electronic energy minimum of $UO_2(H_2O)_5^{2+}$, while the structure Figure 2b has much lower Gibbs energy than the Figure 2a structure. The two structures significantly differ in the $U-O_{eq}$ bond distances, suggesting a large entropy contribution to the geometry; Figure 2a has the electronic energy 2.0 kJ/mol lower than Figure 2b, while the former has the Gibbs energy 6.4 kJ/mol higher than the latter. Therefore, the accuracy of the Gibbs energy calculation using the electronic energy minimum is estimated to be, at best, 10 kJ/mol.

Similar calculations were performed to test the "5 + 1" against the "6" model, and the results are shown in Figure 3. It was found that the 6-fold uranyl(VI) lies 42.9 kJ/mol above the 5-fold uranyl(VI), and there is virtually no activation barrier; transition states lie very close to the intermediate states. Small negative activation energy in Figure 3 is a computational artifact of using the electronic energy minimum to calculate the Gibbs energy. One can also obtain negative activation energy if one picks the gas-phase energy from the PCM-based reaction energy calculation, but this does not make much chemical sense. It is merely a computational artifact and is not an indication of "an error in the computation" as Rotzinger[26] criticized regarding our previous work[27] on Th(IV) water-exchange reaction. Similarly, in the present study, the gas-phase energy of the transition-state TSB23 (Figure 3) is lower than that of the intermediate B3, but this fact does not have any important chemical meaning. Again, the result is in good agreement with what was previously obtained by Vallet et al.[5] except that the B1 model was not tested in their study. There is a same $n + 1$ model problem here and the $H_I \cdots O_{II}$ distance is too short, suggesting that the stability of the B1 is overestimated. Therefore, although the calculated energy difference between the B1 and the B3 is 42.9 kJ/mol, the actual energy difference between the 5-fold and the 6-fold uranyl(VI) is supposed to be slightly smaller than this value.

The activation Gibbs energy of the water-exchange reaction via a dissociative (*D*-) and an associative (*A*-) pathway obtained in this study are $\Delta G^{\ddagger} = 54.6$kJ/mol and $\Delta G^{\ddagger} = 42.4$ kJ/mol, respectively. The experimental number for the same reaction obtained by ^{17}O NMR is 38.1 kJ/mol[28] and is in reasonable accord with the theoretically obtained value on the *A*-mechanism. These values are not directly comparable with those in previous theoretical works as those works did not consider A2 and B1 as possible intermediates. However, the activation free energy between the A1 and the A3 (via A2[29]) obtained in this study is 53.0 kJ/mol and agrees well with previously obtained $\Delta U = 59.2$ kJ/mol by Vallet et al. and also with Car–Parrinello MD simulation result obtained by Bühl et al. where activation free energy is $\Delta A = 45.2$ kJ/mol. For the *A*-mechanism, the

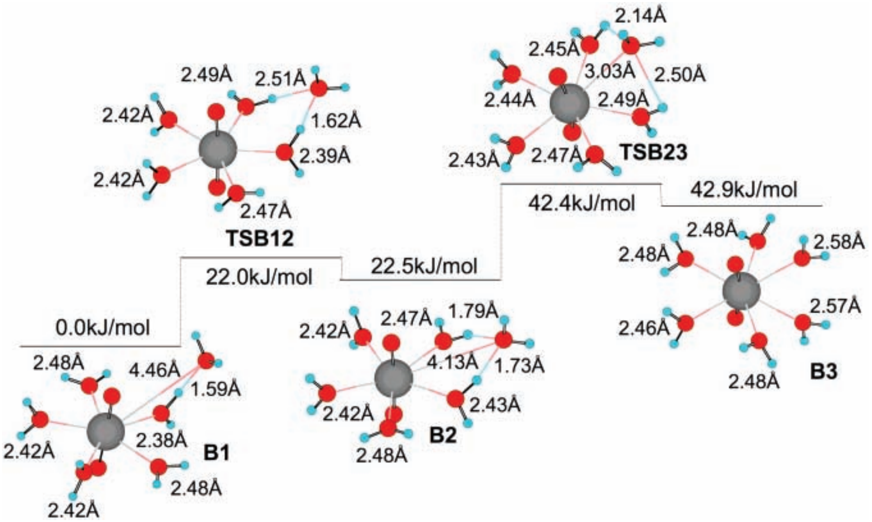

Figure 3. The optimized structures and the Gibbs energies in the aqueous phase of the 5-fold and the 6-fold uranyl(VI) hydrate and the transition states between them. The Gibbs energy value is relative to the complex B1.

activation Gibbs energy between the 5-fold B2 and the 6-fold B3 obtained in this study is $\Delta G = 19.9$ kJ/mol and agrees well with $\Delta U = 18.7$ kJ/mol obtained by Vallet et al. and $\Delta A = 28.0$ kJ/mol by Bühl et al.

The results obtained in this study suggest that although the 4-fold intermediate is energetically more favorable than the 6-fold intermediate, the activation energy of the water-exchange reaction is lower to pass through an *A*-mechanism than through a *D*-mechanism. However, the $n + 1$ model tends to overestimate the stability of the complex, and the energies of both $5 + 1$ and $4 + 1$ complexes are slightly underestimated. This effect arising from the $n + 1$ model was estimated to be only ~1 kJ/mol but could be much larger in practice. One example is the case of uranyl(VI) monosulfato complex UO_2SO_4(aq), where the B3LYP calculations show that bidentate coordination is preferred above unidentate coordination by 14.9 kJ/mol, while the extended X-ray absorption fine structure (EXAFS) measurements clearly show sulfate unidentate coordination.[30] For the molecular modeling in the DFT calculations, the unidentate UO_2SO_4(aq) has four waters coordinated in the first shell, while the bidentate UO_2SO_4(aq) has three waters in the first shell and one water in the second shell. Therefore, it has the same $n + 1$ problem, and the stability of the bidentate model is overestimated while this is not the case for the unidentate model. It is perhaps difficult to discuss whether uni- or bidentate coordination is likely, using the B3LYP calculations, unless the second coordination shell is treated more properly.

From HEXS measurements of the uranyl(VI) hydrate in dilute perchlorate solution, Soderholm et al. concluded that the 4-fold uranyl(VI) stays only 5.0 kJ/mol above the 5-fold uranyl(VI) and ruled out the existence of the 6-fold uranyl(VI) hydrate.[22] The energy difference between the 4-fold and the 5-fold uranyl(VI) hydrates obtained by Soderholm et al. is much smaller than the value obtained in this work, 29.9 kJ/mol. Although the calculated energy difference can easily vary with different solvation model or different solute radius,[13] the experimental value obtained by Soderholm et al. is also obtained with several assumptions such as using Mulliken charge on coordinating water, and these assumptions are not 100% justified. This point needs further investigation from both theory and experimental sides.

Similar calculations have been extended to UO_2^+ and NpO_2^{2+} hydrates. Spin−orbit effect, which is negligible for the closed-shell UO_2^{2+} and which becomes important for UO_2^+ and NpO_2^{2+} ions both of which have $5f^1$ electronic configurations, was neglected because this effect is expected to be canceled between the two complexes just having different hydration numbers. Only two types of stable complexes 5 and $4 + 1$ (A3-type structure in Figure 1) have been identified for both UO_2^+ and NpO_2^{2+}. The coordinates of the complexes are given in the Supporting Information. The energy difference between the 5-fold and the 4-fold is 34.4 kJ/mol and 43.2 kJ/mol for UO_2^+ and NpO_2^{2+}, respectively, preferring the 5-fold. The corresponding number for UO_2^{2+} is 54.3 kJ/mol. So, the energy difference between the 5-fold and the 4-fold decreases ~10 kJ/mol as atomic number increases from 92 (U) to 93 (Np) and decreases ~20 kJ/mol as the oxidation state changes from VI (UO_2^{2+}) to V (UO_2^+). The EXAFS measurements of NpO_2^{2+} and NpO_2^+ hydrates by Reich et al.[31] show that, by the reduction from Np(VI) to Np(V), the hydration number decreases by nearly 1.0. It is thus reasonable to assume that the hydration number is 5 for NpO_2^{2+} and 4 for NpO_2^+. Unfortunately, there is no comparative data available for UO_2^+ because of a rapid disproportionation of UO_2^+ hydrate. However, since the change in the oxidation state (from VI to V) has a larger effect (~20 kJ/mol) than the change in the atomic number (U to Np, ~10 kJ/mol), it might be possible that the UO_2^+ ion prefers the 4-fold coordination.

In summary, precursors, intermediates, and transition states were identified for the 4-, 5-, and 6-fold uranyl(VI) hydrates at the B3LYP level using small-core ECP on uranium and oxygen. The result suggests the 5-fold uranyl(VI) to be the most stable. The hydration number still remains 5 for NpO_2^{2+} ion but might be 4 or 5 for UO_2^+ ion. It was found that the $n + 1$ model underestimates the An−O_{II} distance and thereby overestimate its energetic stability. The 4-fold uranyl(VI) hydrate stays closer to the 5-fold complex than the 6-fold complex does, but the water-exchange reaction of the 5-fold uranyl(VI) takes place through an associative mechanism, and this process is very rapid.

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Supporting Information Available: Coordinates of all precursors, intermediates, and transition states. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(29) Transition state in ref 5 Figure S3b is close to Figure 1 TSA12 in this article and perhaps corresponds to the transition state between A1 and A2 rather than between A1 and A3. We were not able to identify the transition state between A1 and A3. Similarly, we were also not able to identify the transition state between B1 and B3.

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