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Photochemical Reduction of UO_2^{2+} in the Presence of Alcohol Studied by Density Functional Theory Calculations

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A well-known photochemical process of $U^{VI}O_2^{2+}$ reduction to $U^{V}O_2^{+}$ in the presence of alcohols was studied by density functional theory (DFT) calculations. It was found that the first process which takes place is a photoexcitation of the ground-state UO_2^{2+} to the triplet excited state ($^*UO_2^{2+}$) followed by a significant shortening of the $^*UO_2^{2+}$-to-alcohol $O_{ax}-H$ distance. A charge transfer from $^*UO_2^{2+}$ to alcohol and hydrogen abstraction takes place in the following step. Consequently, $U^{VI}O_2^{2+}$ gets reduced to $U^{V}O(OH)^{2+}$. The photochemical byproduct $R\dot{C}HOH$ acts further as a reducing agent toward UO_2^{2+} to yield UO_2^{+} and RCHO (aldehyde). Only a combination of these two reactions can explain a high quantum yield of this reaction. In the absence of alcohol, the lowest-lying triplet state exhibits a different character, and photoreduction is unlikely to take place via the same mechanism. The present results agree well with recent experimental finding [*J. Am. Chem. Soc.* **2006**, *128*, 14024] and supports the idea that the $O_{ax}-H$ linkage between UO_2^{2+} and the solvent molecule is the key to the photochemical reduction process.

Introduction

The history of the photochemistry of UO_2^{2+} ion dates back to early 19 th century when uranyl(VI) oxalate was found to decompose under light irradiation. But the most extensive work on uranium photochemistry was perhaps performed during World War II through the Manhattan Project to seek the possibility of uranium isotope enrichment.[1] In the 1970s, after development of laser technology, the photochemistry of uranium had again attracted wide interest from the chemists, and the mechanism of photochemical reactions was studied quite in detail.[2]

The UO_2^{2+} ion in aqueous solution can be photochemically reduced to UO_2^{+} (and eventually to U^{4+} through disproportionation) in the presence of alcohols such as methanol and ethanol.[1-4] This reaction can be applied to the selective separation of uranium from other actinides and from the fission products in the spent nuclear fuel reprocessing[5] although some difficulties remain for practical applications. A proposed mechanism for the photochemical reduction of uranyl(VI) involves abstraction of hydrogen atom from RCH_2OH molecule by the photoexcited UO_2^{2+} entity ($^*UO_2^{2+}$). Kannan et al.[6,7] have recently demonstrated for an anhydrous methanol solution of the uranyl (VI) phosphine oxide that the photochemical reduction of uranyl(VI) proceeds via the axial oxygen linkage and that this reaction is reversible. Generally, axial oxygen of UO_2^{2+} in aqueous media is unreactive, and the rate of the oxygen exchange reaction is extremely slow.[8-10] The rate of oxygen exchange increases with increasing concentration of uranyl hydroxo dimer complex, $(UO_2)_2(OH)_2^{2+}$.[11] The rate of oxygen exchange also increases under the influence of light because of the elongation of the $U-O_{ax}$ bond in the photoexcited state $^*UO_2^{2+}$.[12-14] The results in alkaline solution are

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giving contradictory results. Clark et al.[15] experimentally and Shamov et al.[16] and Hratchian et al.[17] theoretically studied the oxygen exchange in strong alkaline solution where the uranyl(VI) stay as $UO_2(OH)_4^{2-}$. Clark et al. observed a rapid oxygen exchange in $UO_2(OH)_4^{2-}$, and Shamov et al. argues that the oxygen exchange in $UO_2(OH)_4^{2-}$ occurs via the formation of an intermediate species $UO_3(OH)_3^{3-}$ via formation of penta-hydroxo complex $UO_2(OH)_5^{3-}$. However, Szabo et al.[11] did not experimentally find (as shown in Figure S1 in ref11.) the type of exchange reaction claimed by Clark et al.[15] and conclude that the reactions observed by Clark et al. are experimental artifact. Recently, the reactivity of the axial oxygen of the uranyl group is attracting growing attention. Arnold and co-authors[18] have successfully synthesized the oxo group silylated uranyl(V) complex and have proved that the uranyl(VI) axial group can actively participate in chemical reactions. The work by Arnold et al. has a large impact on the uranium chemistry as discussed by Boncella.[19] There are also increasing interests in the catalytic behavior of uranium, and it was recently published as a review article by Fox et al.[20] Catalytic behavior of uranium is not limited to the laboratory scale but may also take place in natural environment either through biological[21] or through geological processes.[22]

Recent studies by Kanann et al.[6,7] focused the spotlight again on the photochemical reduction of uranyl(VI) ion. Kannan et al. brought the discussions to the new stage by experimentally pointing out that the axial linkage O_{ax}−H is the key to the photochemical processes. The complete understanding of the photochemical reduction mechanism and the properties of the excited states are, however, difficult solely by experimental methods. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are potent for such a purpose. Several recent studies discussed the reliabilities of the TD-DFT method for the system containing the uranyl(VI) group.[13,14,23] For $[UO_2Cl_4]^{2-}$, Pierloot et al.[23] reported that the TD-DFT tends to overestimate the covalency of the uranyl-chlorine bond and that the highest occupied molecular orbital (HOMO) shows high chlorine character, which is not in agreement with CASPT2 calculations nor with spectroscopic observation.[24] Pierloot et al., however, concluded that "we believe that this work presents a convincing first example of the strength of the two-component relativistic TDDFT approach for the research on spectroscopic properties of heavy element compounds". In fact, Réal et al.[13,14] have successfully studied the photoexcited states of UO_2^{2+} as well as the axial oxygen exchange reaction in UO_2^{2+} within the framework of DFT and TD-DFT. Wiebke et al.[25] have also applied the TD-DFT method to calculate the absorption spectra of uranyl (VI) complexes.

In this article, I will focus on the mechanism of the photochemical reduction of UO_2^{2+} in the presence of methanol and ethanol by using DFT and TD-DFT methods. The apical linkage of UO_2^{2+} with alcohol molecules will be the main focus of this study, and the excited states which are the key to photochemical reactions have been identified.

Computational Methodology

All the calculations were performed in solvent (H_2O, CH_3OH, and CH_3CH_2OH) using the Gaussian 03 program[26] employing the DFT method with Becke's three-parameter hybrid functional[27] and Lee−Yang−Parr's gradient corrected correlation functional (B3LYP)[28] through the use of the conductor-like polarizable continuum model (CPCM)[29] using UAHF radii.[30] The energy-consistent small-core effective core potential (ECP) and the corresponding basis set suggested by Dolg et al. were used for uranium,[31] oxygen,[32] and carbon.[32] The most diffuse basis functions on uranium with the exponent 0.005 (all s, p, d, and f type functions) were omitted to make the convergence of the electronic wave function much faster, which generally has only little effect (less than 1 kJ/mol) to the total energy, according to the previous study.[33] The d-function on oxygen and the g-function on uranium have been added. For hydrogen, a 6-311++G** basis was used.[34] The Gibbs energy correction to the electronic energy was calculated at the B3LYP level from the vibrational energy levels in aqueous phase and the molecular partition functions. In few cases, a single and small imaginary frequency remained in the final geometry, but such small imaginary frequencies are known to be often merely computational (numerical) artifacts of the solvent models.[35] In case imaginary frequency is present, it was assured that the imaginary modes describe rotational movements within the ligands (e.g., rotation of coordinating water); hence confirming that the presence of imaginary frequencies does not

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largely affect the discussions. The pressure correction to the entropy using the pressure parameter of $p = 1354$ atm, as proposed by Martin et al.,[36] was not considered in this study. Spin−orbit effect and the basis set superposition error (BSSE) corrections were also not considered. The transition state was identified through a single imaginary frequency that describes the translation movement across the energy barrier.

Non-equilibrium TD-DFT calculations[37,38] were performed in the solvent phase producing both singlet and triplet excited states. Ten singlet and ten triplet excited states were determined using the ground states geometries.

Results and Discussions

Ground State and Triplet State Geometries. Most of recent theoretical studies[39−55] agree that the UO_2^{2+} aquo ion has five water molecules in the first coordination sphere, although 4-fold coordination may also occur.[56−58] In this study, the penta-aquo complex was used as a model of the UO_2^{2+} ion.

The complexes optimized are penta-aquo uranyl(VI) $[UO_2(OH_2)_5]^{2+}$ linked with a single CH_3OH (**1**, **2**), CH_3CH_2OH (**3**, **4**, **5**), and H_2O (**6**) molecule via an axial oxygen. These complexes are the model of the uranyl (VI) ion in the presence of CH_3OH (**1**, **2**) or CH_3CH_2OH (**3**, **4**, **5**) and that in the absence of alcohol (**6**). For CH_3OH and CH_3CH_2OH, the axial link was made via either a hydrogen atom of the methyl group (**1**, **3**, **4**) or that of the OH group (**2**, **5**). The ground-state geometries of six complexes (**S1**−**S6**) were obtained in the solvent (methanol, ethanol, water) at the B3LYP level. The surrounding solvent was changed in accordance with the linked molecule. The lowest lying triplet state geometries of the same complexes were obtained in the solvent using the unrestricted Kohn−Sham formalism at the B3LYP level (**T1**−**T6**). All the complexes studied are summarized in Table 1, and the structures of four major complexes (**S1**, **S6**, **T1**, and **T6**) are given in Figure 1. The coordinates of all complexes are given in the Supporting Information.

At the ground-state geometry, in all cases, there is only a weak hydrogen bond between the solvent molecules and the axial oxygen. The $O_{ax}\cdots H$ distance varies from the shortest 2.126 Å (**S6**) to the longest 3.662 Å (**S3**). It is still a matter of discussion whether or not there is an apical water linkage to UO_2^{2+} in aqueous solution. Fully *ab initio* calculations,[43] combined quantum chemical + molecular dynamics simulations,[47] and QM/MM calculations[59] indicated that there is no apical water linkage, while Monte Carlo simulation based on model potential,[44] DFT calculations,[60] and CPMD calculations[61] found the presence of such waters. The results depend on initial geometries, molecular potentials, and also whether the method used is dynamical or static. In case of alcohol, an apical linkage is even weaker than that with water. The $O_{ax}\cdots H$ distances between axial oxygen and alcohol is overall long, showing that there is only a weak interaction between the uranyl (VI) oxygen and alcohol. To estimate the strength of the apical linkage, the $O_{ax}\cdots H$ distance in **S1** and **S6** were changed from their equilibrium distances of 2.972 Å and 2.126 Å, respectively, to 5.000 Å, and the energies (including solvation energy but excluding thermal correction and entropy) of the complexes were compared with those at the equilibrium distances. In the dissociated complex, the energy increased only by 0.7 and 0.2 kJ/mol for **S1** and **S6**, respectively. Such small energy values, which are even comparable to kinetic energy at room temperature, shows that there is no distinct hydrogen bond to the axial oxygen of UO_2^{2+}. But it does not imply that such an $O_{ax}\cdots H$ link is not formed in a dynamical time scale. Therefore in the following discussion it is assumed that there is an $O_{ax}\cdots H$ linkage.

The $O_{ax}\cdots H$ distance is much longer when the axial linkage is formed via the methyl group than via the OH group. The $O_{ax}\cdots H$ distance is 2.972 Å in methyl group mediated $O_{ax}\cdots H$ linkage (**S1**), while the same number to compare in the OH group mediated $O_{ax}\cdots H$ linkage is 2.164 Å (**S2**). The Gibbs energy of **S1** is 12.5 kJ/mol lower than **S2** indicating that the methyl group linked complex is slightly more stable than the OH group linked complex. However, the energy difference of 12.5 kJ/mol is within the error of this type of calculations as discussed

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Table 1. List of Complexes **1**−**4** in Singlet Ground States (**S1**− **S6**) and Lowest-Lying Triplet States (**T1**− **T6**) and $O_{ax}\cdots H$ Distances[a]

		solvent					
		CH_3OH		CH_3CH_2OH			H_2O
link to uranyl oxygen via		CH_3	OH	CH_3	CH_2	OH	H_2O
singlet ground state	complex	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
	$O_{ax}\cdots H$ distance	2.972	2.162	3.662	2.732	2.164	2.126
first triplet state	complex	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**
	$O_{ax}\cdots H$ distance	1.012	1.007	0.996	1.019	1.013	2.108

[a] Unit in Ångström.

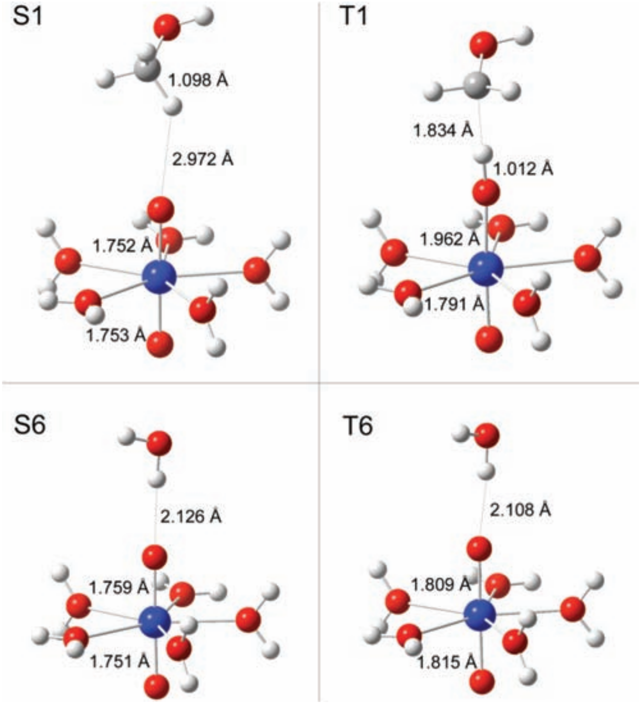

Figure 1. Structures and major interatomic distances ($U-O_{ax}$, $O_{ax}\cdots H$, C−H) of the ground state (**S1**, **S6**) and the lowest-lying triplet state (**T1**, **T6**) of the UO_2^{2+} penta-hydrate linked with ethanol (**1**) and water (**6**).

elsewhere recently.[53,55,62] Therefore, it is not possible to conclude which linkage is energetically more preferred. Both lie close in energy.

Similar calculations were made using ethanol as solvent. The linkage between ethanol and the uranyl was tested for all possible cases, namely CH_3 (**3**), CH_2 (**4**), and OH (**5**). In the ground-state geometries, only a weak bonding between ethanol and the uranyl was found. The $O_{ax}\cdots H$ distances are 3.662 Å (**S3**), 2.732 Å (**S4**), and 2.164 Å (**S5**), and the relative Gibbs energies of these three complexes are 0.0 (**S3**), 1.6 (**S4**), and 6.8 (**S5**) kJ/mol, slightly preferring **S3** and **S4** above **S5**. The OH group mediated linkage has much shorter $O_{ax}\cdots H$ distances, but from the energetic point of view, methyl group mediated linkage is slightly more preferred. But again, all of **S3**−**S5** lie close in energy, and it is hard to make a definitive conclusion which of **S3**− **S5** is the most stable.

The singlet to triplet transition is generally not allowed according to the spin selection rule, but because of the spin−orbit coupling and internal conversion it may be observed in practice with low molar absorption coefficients of $\varepsilon < 1\ dm^3\ mol^{-1}\ cm^{-1}$. The geometries of the first triplet states were obtained in the unrestricted Kohn−Sham scheme. It can be seen from Table 1 and Figure 1 that there is a clear distinction between the geometries of the first triplet states of the alcohol system (**T1**−**T5**) and that of the water system (**T6**). In the former complexes, the UO_2^{2+} entity abstracts a hydrogen atom from the methyl group or from the OH group. Consequently, the $O_{ax}\cdots H$ distances in **T1**−**T5** are much shorter (0.996 to 1.013 Å) compared to those in the singlet states, while the $O_{ax}\cdots H$ distance in **T6** (which is in the $^3\Phi_g$ state) remains essentially the same as that in the corresponding singlet state (2.108 Å in **T6** versus 2.126 Å in **S6**).

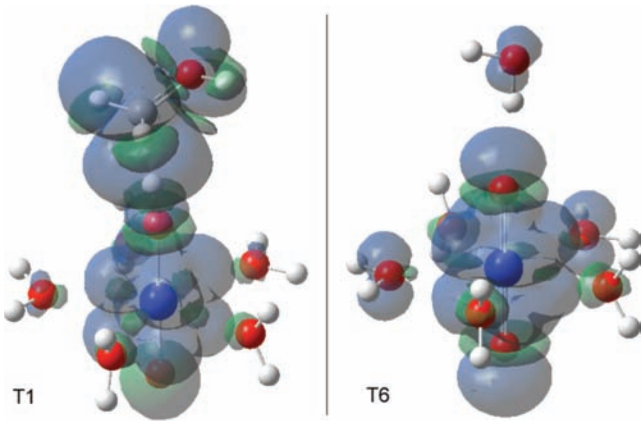

Figure 2. Contour plot of the spin density of the lowest-lying triplet state of uranyl penta-hydrate linked with ethanol (**T1**) and water (**T6**) (isovalue of the plot is 0.0004).

To study this point further, Mulliken population analysis has been performed. As shown by the spin density surface of the complex in Figure 2, the Mulliken atomic spin density of **T1** (in which the total spin density is 2.00) is centered on "UO(OH)" (1.06) and "CH_2OH" (0.88) entities roughly in a half-to-half fashion. The spin density of **T6** (total spin density is 2.00) is centered virtually only on "UO_2" (1.96). It shows that in the **T1** state there is a significant charge transfer from uranyl to methanol, while in the **T6** state there is no charge transfer from UO_2^{2+} entity to the solvent. The Mulliken atomic charges of **S1** and **T1** were also compared, and it was found that the "UO_2" in **S1** and "UO(OH)" in **T1** have nearly the same net charges of 1.11 and 1.08, respectively. These results clearly indicate that by the excitation from **S1** to **T1** there is an electron transfer from methanol to uranyl (VI) nearly by 1.0 e so that uranium(VI) is practically reduced to uranium(V) in **T1**.

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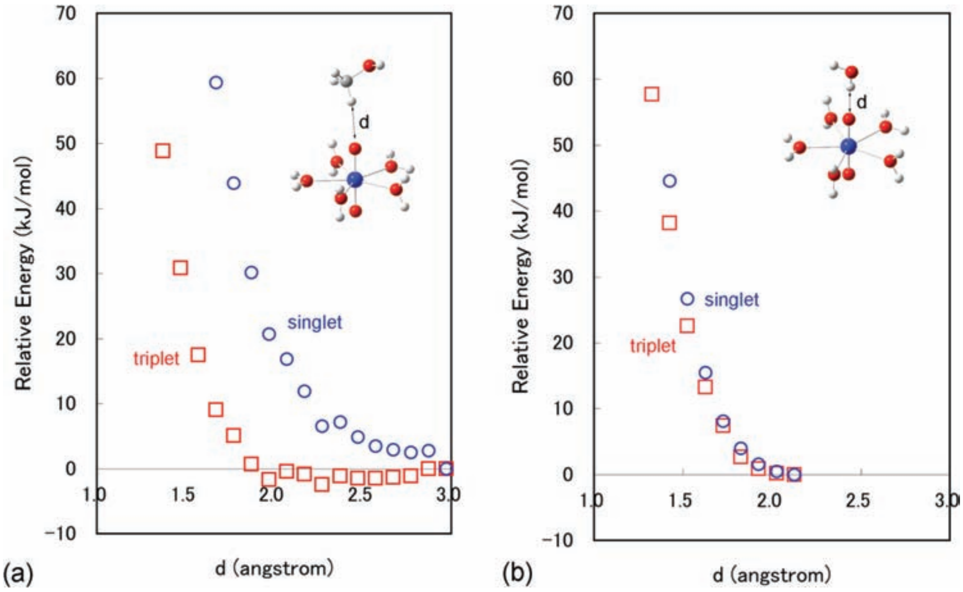

Figure 3. Potential energy curve of the **S1** (a) and **S6** (b) along the $O_{ax}\cdots H$ coordinate at the singlet (blue) and the lowest-lying triplet state (red). The zero-point of the energy is set to the energy at the singlet equilibrium geometry.

Singlet to Triplet Excitation. To study more of the nature of the lowest-lying triplet states and transitions from the ground states to the triplet states, vertical transitions from singlet to triplet states have been studied. By vertically exciting **S1** to the triplet state, namely, by calculating the triplet state energy and the orbital population using the singlet **S1** geometry in the Kohn−Sham formalism, the spin density on UO_2^{2+} and CH_3OH entity was found to be 1.87 and 0.11, respectively. Similarly, by vertically exciting **S6** to the lowest-lying triplet state, the spin density on UO_2^{2+} and H_2O entity was found to be 1.96 and 0.00, respectively. So the vertical excitation from **S6** to the lowest-lying triplet state is likely to occur via metal centered charge transfer (MCCT) or via metal-to-ligand charge transfer (MLCT) within the UO_2^{2+} unit (thereby the spin density localized almost on UO_2^{2+}), while in the **S1** case there is a partial electron outflow from the apical solvent to the uranyl.

Vertical transitions from singlet to triplet states were studied also by TD-DFT calculations. TD-DFT results show the five lowest triplet bands lying in 500−472 nm (**S1**), and in 493−361 nm (**S6**). In **S1**, the HOMO is CH_3OH centered, and HOMO-2 and HOMO-5 are $[UO_2(OH_2)_5]^{2+}$ centered. The lowest unoccupied molecular orbital (LUMO), LUMO + 1, and LUMO + 2 are all uranium centered. Isodensity plots of these molecular orbitals are given in the Supporting Information, Figure S1. The singlet to triplet excitation occurs by the excitation from these occupied MOs (HOMO to HOMO-5) to unoccupied MOs (LUMO to LUMO + 2), so that the excitation has mainly U to O_{ax} MLCT character but partially involving uranyl to solvent charge transfer. In **S6**, the HOMO is apical water centered and HOMO-1, HOMO-5, HOMO-6 are $[UO_2(OH_2)_5]^{2+}$ centered. The LUMO, LUMO + 1, LUMO + 2, and LUMO + 3 are uranium centered. Isodensity plots of these molecular orbitals are given in the Supporting Information, Figure S2. For the first four excited states, the excitation occurs within the uranyl unit. The fifth excitation at 361 nm occurs by uranyl to solvent charge transfer. The absolute values of vertical excitations energies obtained by TD-DFT calculations strongly depend on the type of functionals and are generally far too low compared to CASPT2 values.[23] For a quantitative discussion of the excitation energies, a more sophisticated theory with proper treatment of spin−orbit coupling is indispensable. But it is also known that the TD-DFT calculations can provide qualitative pictures of the excited states geometries and energies.[14,23] In the present study, both the Kohn−Sham DFT and TD-DFT calculations provide essentially similar pictures of the singlet to triplet excitations. The lowest lying triplet states are mostly MCCT and MLCT states although some contribution from uranyl to solvent charge transfer was also found. It is, however, not very clear from these results why the hydrogen abstraction takes place only by **S1**−**S5** to **T1**−**T5** transitions and not by the **S6** to **T6** transition.

The vertical excitation energies obtained for the lowest four excitations of **S6** (493−435nm) using TD-DFT are not in good agreement with the values obtained by Réal et al.[13] using TD-DFT (590−288 nm). Réal et al. made a systematic investigation of different levels of theories and therefore simple molecular model without inclusion of equatorial waters have been used. Therefore, the U−O_{ax} distances in the present calculations are slightly longer (~0.06 Å) than those obtained by Réal et al., and the first excitation energy, therefore, is higher in the present calculations.

Figure 3 describes the energy profiles of **S1** and **S6** versus change in the $O_{ax}\cdots H$ distance. The potential energy curve of the singlet state was studied keeping the geometries of $[UO_2(OH_2)_5]^{2+}$ and the solvent molecules (CH_3OH and H_2O) to be rigid and changing only the $O_{ax}\cdots H$ distance. The energies relative to the equilibrium $O_{ax}\cdots H$ distance of 2.972 Å (**S1**) and 2.126 Å (**S6**) are shown as blue circles in Figure 3. A similar potential energy curve was plotted also for the triplet state by vertically exciting singlet states to the lowest-lying triplet states, which are shown as red squares in the same figure. The zero-point of the energy was set to the triplet energy at the singlet equilibrium geometry. In Figure 3, it can be seen that by the excitation from the ground-state to the lowest-lying triplet state, the optimal $\mathrm{O_{ax}\cdots H}$ distance changes significantly for the **S1** case but not for the **S6** case. In the **S1** case, in going from singlet to triplet state, there is a significant shortening of the $\mathrm{O_{ax}\cdots H}$ distance. The triplet energy curve (Figure 3a, red) has a minimum at the $\mathrm{O_{ax}\cdots H}$ distance around 2.0 Å and stands between **S1** and **T1** in which the $\mathrm{O_{ax}\cdots H}$ distances are 2.972 Å and 1.012 Å, respectively. The vertical excitation of **S1** occurs only through MLCT and MCCT, as discussed earlier, while in **T1** there is clearly a charge transfer from uranyl to the solvent; therefore, these two triplet states are clearly different electronic states. The intersection of the two triplet states occurs as a result of the shortening of the $\mathrm{O_{ax}\cdots H}$ distance.

Finally, the dissociation of the uranyl-alcohol cluster (**T1**) into $\mathrm{U(V)O(OH)}^{2+}$ + $\mathrm{H\dot{C}HOH}$ fragments was studied by changing the $\mathrm{H\cdots C}$ distance from the equilibrium distance (1.834 Å) to 5.000 Å. By the lengthening of the $\mathrm{H\cdots C}$ distance, the energy of the complex increased by 26.8 kJ/mol. In the dissociated complex, Mulliken spin density on "UO(OH)" and "$\mathrm{CH_2OH}$" fragments are 1.01 and 0.99, respectively, and almost equally localized on two dissociated units, clearly showing uranium(V) character in the former and radical character in the latter. The photoreduction completes with the dissociation into $\mathrm{U(V)O(OH)}^{2+}$ and $\mathrm{H\dot{C}HOH}$ fragments.

From the preceding discussions, the following reaction chains can be proposed for the photochemical reduction of $\mathrm{UO_2}^{2+}$ by alcohol: The first reaction which takes place is photoexcitation of the ground-state $\mathrm{UO_2}^{2+}$ to the triplet excited state $\mathrm{*UO_2}^{2+}$. The photoexcited $\mathrm{*UO_2}^{2+}$ attracts an alcohol molecule, and hydrogen atom abstraction from the alcohol takes place, by which charge transfer from $\mathrm{*UO_2}^{2+}$ to the solvent also occurs. Consequently, $\mathrm{U^{VI}O_2}^{2+}$ gets reduced to $\mathrm{U^{V}O(OH)}^{2+}$.

$\mathrm{U^{V}O(OH)}^{2+}$ is likely to go through disproportionation because $\mathrm{U^{V}O_2(CO_3)_3}^{5-}$ is so far the only known U(V) species to be stable in aqueous solution.[63] A disproportionation mechanism of $\mathrm{UO_2}^{+}$ involving protonated species $\mathrm{U^{V}O(OH)}^{2+}$ as proposed by Kern et al.[64] was soon discounted by Duke et al.,[65] and a more recent DFT study by Steele et al.[66] suggested that the disproportionation of $\mathrm{UO_2}^{+}$ takes place first by a formation of a cation−cation complex followed by protonation of axial oxygens.

The reduction of $\mathrm{UO_2}^{2+}$ by hydrogen[67,68] and hydrogen abstraction from $\mathrm{H_2O}$ by $\mathrm{UO_2}^{2+}$[14] was studied by quantum chemical calculations in the absence of alcohol. The reaction was found to be highly endergonic with large contribution from the solvation energy. Réal et al.[14] extensively studied this reaction as a possible reaction pathway of the photoinduced oxygen exchange reaction in the uranyl(VI). From the structures, energies, and spin density of the lowest-lying triplet states obtained in the present study, it can be concluded that the photoreduction of uranyl(VI) via the axial $\mathrm{O_{ax}\cdots H}$ linkage is less probable to take place when water instead of alcohol is located at the apical site.

Further U(VI) Reduction by the Radicals. According to Bell et al.,[5] the quantum efficiency to yield U(IV) from U (VI) through photoreduction in 3 M $\mathrm{H_2SO_4}$ and in 0.5 M $\mathrm{HNO_3}$ solution all exceed 0.5 (ϕ (U^{4+}) > 0.5). Theoretically speaking, if photoreduction takes place only by the reduction from U(VI) to U(V) followed by disproportionation 2 U(V) → U(VI) + U(IV), ϕ (U^{4+}) cannot exceed 0.5. To overcome this contradiction, Nagaishi et al.[4] proposed another reduction mechanism, in parallel to the photoreduction U(VI) → U(V), which is $\mathrm{R\dot{C}HOH}$ reacting with $\mathrm{UO_2}^{2+}$ to yield RCHO (aldehyde), $\mathrm{UO_2}^{+}$, and H^{+}.

$$\mathrm{U^{VI}O_2}^{2+} + \mathrm{R\dot{C}HOH} \rightarrow \mathrm{U^{V}OOH}^{2+} + \mathrm{RCHO}$$

This reaction is likely to take place for R = H, $\mathrm{CH_3}$ from the thermodynamical point of view. The reduction potential versus normal hydrogen electrode $E°$ is −1.18 V and + 0.088 V for HCHO, $\mathrm{H}^{+}/\mathrm{H\dot{C}HOH}$, and $\mathrm{UO_2}^{2+}/\mathrm{UO_2}^{+}$ couples, respectively.[69,70] In the following, $\mathrm{UO_2}^{2+}$ reduction by $\mathrm{H\dot{C}HOH}$ is discussed.

The precursor, transition state, and the successor of the $\mathrm{UO_2}^{2+}$ interacting with $\mathrm{H\dot{C}HOH}$ have been identified, and they are shown in Figure 4. The coordinates of the complexes are given in the Supporting Information. The precursor and the successor that have been assumed here are $\mathrm{UO_2}^{2+}$ penta aquo ion linked with $\mathrm{H\dot{C}HOH}$, and $\mathrm{UO(OH)}^{2+}$ linked with HCHO, respectively. One water molecule was added between $\mathrm{H\dot{C}HOH}$ and axial oxygen, so that the proton transfer is buffered by water molecule and that the reaction proceeds via an intermolecular process. The Gibbs energy of the successor complex is 122 kJ/mol below the precursor and therefore suggests that this redox reaction is possible from the thermodynamic point of view. One transition state has been identified which describes a proton transfer from the buffering water to the axial oxygen. The transition states lies 76 kJ/mol below the precursor in energy. The energy

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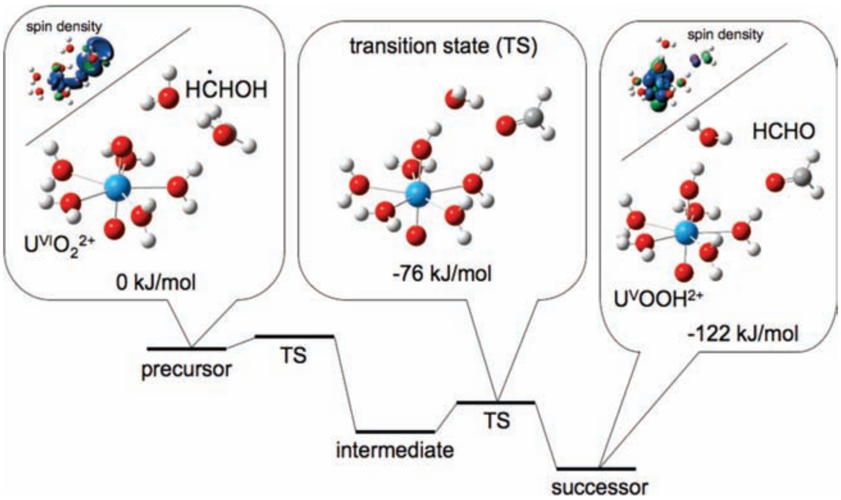

Figure 4. Precursor, successor, and the transition state of UO_2^{2+} interacting with $\mathrm{H\dot{C}HOH}$. Spin density of the complexes are shown for the precursor and the successor.

of the transition state is far below that of the precursor, and this can not be the transition state which directly connects the precursor and the successor. Presumably, there is another transition state that describes the hydrogen abstraction movement, and the rate dominating reaction is therefore a proton transfer from $\mathrm{H\dot{C}HOH}$. However, it was not possible to identify such a transition state, and the reaction proposed here remains only hypothetical.

The spin density of the precursor and the successor are also shown in Figure 4. The sum of spin densities is 1.00 for this system. In the precursor complex, the spin density is localized mostly on the $\mathrm{H\dot{C}HOH}$ radical (0.86) while in the successor complex it is localized almost only on the "UO_2" (1.01). This is a strong support that the uranium in the successor complex is already reduced to U(V).

Conclusions

The present study based on DFT and TD-DFT calculations proposes the following stepwise mechanism for the photochemical reduction of UO_2^{2+} in the presence of alcohol.

(1) Formation of a weak apical $O_{ax}\cdots H$ linkage between UO_2^{2+} and alcohol. (2) Photoexcitation of the UO_2^{2+} entity to the triplet excited state. (3) Significant shortening of the $^*UO_2^{2+}$-to-alcohol apical $O_{ax}\cdots H$ linkage. (4) Charge transfer from the photoexcited $^*UO_2^{2+}$ to alcohol, and hydrogen abstraction from alcohol. (5) Dissociation of the uranyl-alcohol cluster into $\mathrm{U(V)O(OH)^{2+}} + \mathrm{R\dot{C}HOH}$ fragments. (6) Formation of a $UO_2^{2+}-\mathrm{R\dot{C}HOH}$ cluster. (7) Intermolecular proton transfer from $\mathrm{R\dot{C}HOH}$ to UO_2^{2+}, and formation of $\mathrm{U(V)O(OH)^{2+}} + \mathrm{RCHO}$ fragments.

The present study points out the importance of the "axial linkage" which potentially enhances the reactivity of the uranyl (VI) oxygen. The reaction mechanism proposed here is not only consistent with previous experimental findings (Burrows 1974, Nagaishi 2002, Kannan 2006) but also provides further complementary information. It demonstrates that the photoexcitation of the uranyl(VI) involving redox reactions can be approximately modeled in the framework of DFT and TD-DFT with reasonable computational effort.

The present study applied the DFT method with the use of a limited size of basis set neglecting both BSSE correction and spin−orbit effect. One may argue that the standard DFT is not capable of accounting properly for the dispersive interaction and leaves concerns to the results presented here. Several recent studies[71] successfully studied the hydrogen abstracting interaction in the framework of DFT. Nevertheless, for further quantitative understanding of the reaction energetics and reaction kinetics, it is mandatory that more sophisticated calculations including spin−orbit effect are tested on the present system. This point is worthwhile of further investigation.

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Supporting Information Available: Coordinates of all complexes. Molecular orbitals of **S1−S6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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