論文題目　　　Geochemistry on Uranyl: A Theoretical Study
（理論化学計算によるウラニルの地球環境化学研究）

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## 1. Introduction

The large amount of actinide elements, especially uranium and transuranic elements, is produced in nuclear reactors. The majority of the spent fuel and its decay products are supposed to be disposed in deep geologic repositories. The microscopic elucidation of properties associated with interactions between actinides and naturally-occurring species is crucial to the nuclear waste disposal and its risk and safety assessment in the future. This is also useful to develop remediation techniques for the environments polluted by extensive uranium mining and processing. Understanding actinide geochemistry is intrinsically difficult because various complex processes must be considered simultaneously such as sorption, precipitation/dissolution, redox equilibria, solubility, radiolysis, hydrolysis, humic acid complexation, colloid generation, and the influences of other metal ions and other potential ligands. These varieties of factors affect on the fate and transport properties of actinides in aquifer systems. The thermodynamic models such as Surface Complexation Model (SCM), for example, can describe sufficiently behaviors of metal cations and speciations in aqueous solution if reliable parameters are available such as equilibrium constants of metal surface complex, stoichiometries of surface complex and charge distributions of surface complex. These parameters reflect microscopic information from the complex structures, coordination numbers, and charge distribution. In some cases, however, there are difficulties to obtain precise data in experiments without uncertainty.

The chemistry of actinide elements is experimentally and theoretically challenging area. Experiments must be carried out at shielding conditions for the limited amount of actinide elements. Actinide elements have a variety of accessible oxidation states in natural conditions, and multiple oxidation states of the same element may exist simultaneously. Chemical behaviors of the actinide elements are different depending on their oxidation states. The actinide elements have a characteristic 5f orbital which participates in chemical bonds, while the 4f orbital of lanthanide elements is known to be chemically inert and not to make chemical bonds. This 5f character potentially plays an important role in actinide-containing reactions. The difficulty in theoretical treatments of actinide elements comes from their complex electronic structures, strong correlation, large relativistic effects, and probably coupling of these.

## 2. Objectives

This thesis targets uranium as a representative of actinide elements, and the complex geochemical behaviors of aqueous uranium compounds were investigated in the theoretical standpoint. The objectives of this thesis are to construct and propose theoretical methods for predicting the redox

reactions, adsorption of uranyl(VI) on mineral surfaces, and surface reduction of uranyl (VI) as an extension of preceding studies.

## 3. Reduction of Uranyl(VI)

In chapter 2, the problem previously mentioned on DFT calculations of uranium was re-examined. Some previous works pointed out that DFT was not suitable for actinide chemistry because of failing prediction of reaction energies. This chapter examined a variety of issues mentioned before, and also provided a kind of benchmark study between DFT and MO calculations. Early works modeled the stepwise one electron reduction of uranyl(VI) using bare ions, $U^{VI}O_2^{2+}$, $U^{V}OOH^{2+}$, and $UIV(OH)_2^{2+}$, and pointed out that DFT calculations provided improper reaction energies on the reduction of uranyl(VI) by water. The present study focused on the absence of solvation effect in that works. It was revealed that inclusion of solvation effect by a polarizable continuum model and explicit introduction of coordinated ligands to uranyl(VI) would solve the poor performance in DFT calculations. This is firstly because the solvation energy is large enough to compensate for gas-phase reaction energies, and secondly because the underestimation of the stability of triple bonds of uranyl(VI) would cause also underestimation of the reaction energies. Uranyl(VI) has energetically nearly degenerate $\sigma$ and $\pi$ orbitals. Introduction of proper ligand fields made nearly degenerate orbitals splitted and made it possible to use DFT for redox reactions of uranyl(VI). It is concluded that DFT has no problem on the redox system, but model system without ligand field is the main problem. To sum up, DFT with proper ligand fields are suitable for uranium (actinide) chemistry.

## 4. Binary Uranyl Adsorption Complexes

In chapter 3, the structure of uranyl sorption complexes on gibbsite (pH 5.6 - 9.7) was discussed. Two independent methods, DFT calculations and EXAFS spectroscopy at the U-$L_{III}$ edge, were used. To model the gibbsite surface with DFT, two Al (hydr)oxide clusters , a dimer and a hexamer, were tested. Based on polarization, structure, and relaxation energies during geometry optimization, the hexamer cluster was found to be the more appropriate model. An additional advantage of the hexamer model is that it represents both edges and basal faces of gibbsite. The DFT calculations of (monomeric) uranyl sorption complexes showed an energetic preference for the corner-sharing versus the edge-sharing configuration on gibbsite edges. The energy difference is so small, however, that possibly both surface species may coexist. In contrast to the edge sites, sorption to basal sites was energetically not favorable. EXAFS spectroscopy revealed in all investigated samples the same interatomic distances of the uranyl coordination environment ($R_{U-Oax} \approx 1.80$ Å, $R_{U-Oeq} \approx 2.40$ Å), and towards the gibbsite surface ($R_{U-O} \approx 2.87$ Å, $R_{U-Al} \approx 3.38$ Å). In addition, two U-U distances were observed, 3.92 Å at pH 9.7 and 4.30 Å at pH 5.6, both with coordination numbers of ~ 1. The short U-U distance is close to that of the aqueous uranyl hydroxo dimer, $UO_2(OH)_2$, reported as 3.875 Å in the literature, but significantly longer than that of aqueous trimers (3.81-3.82 Å), suggesting sorption of uranyl dimers at alkaline pH. The longer

U-U distance (4.30 Å) at acidic pH, however, is not in line with known aqueous uranyl polymer complexes. Based on the EXAFS findings, further dimeric surface complexes with DFT were refined. Two structural models were proposed: in the acidic region, the observed long U-U distance can be explained with a distortion of the uranyl dimer to form both a corner-sharing and an edge-sharing linkage to neighboring Al octahedra, leading to $R_{U-U}$ = 4.150 Å. In the alkaline region, a corner-sharing uranyl dimer complex is the most favorable. The U-O path at ~2.87 Å in the EXAFS spectra arises from the oxygen atom linking two Al cations in corner-sharing arrangement. The adsorption structures obtained by DFT calculations are in good agreement with the structural parameters from EXAFS analysis: U-Al (3.394 Å), U-U (3.949 Å), and U-O (2.823 Å) for the alkaline pH model, and U-Al (3.279 Å), U-U (4.150 Å), and U-O (2.743 Å) for the acidic pH model.

## 5. Ternary Uranyl Adsorption Complexes

In chapter 4, the structure of uranyl sorption complexes on gibbsite (pH 5.5 and 9.6) in the presence of silicate was discussed. This chapter is closely related to chapter 3, and is dedicated to investigating influence of coexisting ligands on sorption of uranyl to mineral surfaces. The combination of DFT calculations and EXAFS spectroscopy were again used. Based on the findings in chapter 3, the hexamer cluster was exploited to model adsorption on edge faces of gibbsite. The DFT calculations of uranyl silicate ternary sorption complexes showed a comparable energetic stability for the corner-sharing versus the edge-sharing configuration on gibbsite edges. The energy difference is smaller than those found in binary systems (chapter 3). EXAFS spectroscopy in both samples showed the same interatomic distances for U-$O_{ax}$, U-$O_{eq}$, and U-Al ($R_{U-Oax}$ ≈ 1.80 Å, $R_{U-Oeq}$ ≈ 2.40 Å, $R_{U-Al}$ ≈ 3.38 Å) as those of the binary systems (chapter 3). In addition, two U-Si distances were observed, 3.82 and 3.10 Å at pH 5.5 and 3.07 Å at pH 9.6, both with coordination numbers of ~ 1. The shorter U-Si distance is attributed to contribution from bidentate silicates, and the longer one is from monodentate silicates. Contrary to the observation in the binary systems, the EXAFS spectrum of acidic sample has shorter U-U distance of 3.76 Å, while the alkaline sample provides the longer U-U distance of 4.22 Å. Based on the EXAFS findings, two structural models were proposed by DFT calculations: in the acidic region, the observed combination of short U-U and two U-Si distances can be explained with a soddyite-like structure. In this fragment, two uranyl units are linked by both monodentate and bidentate silicate, leading to $R_{U-U}$ = 3.84 Å, $R_{U-Si}$ = 3.89 Å, and $R_{U-Si}$ = 3.10 Å. In the alkaline region, neighboring corner- and edge-sharing uranyl ions both coordinated by bidentate silicates is the most favorable, giving $R_{U-U}$ = 4.24 Å and $R_{U-Si}$ = 2.98 Å. Due to the coordinations of silicates and gibbsite, EXAFS spectra in both samples clearly show separate U-$O_{eq}$ shells, which is not observed in the binary systems.

## 6. Reduction of Uranyl(VI) by Fe(II)

In chapter 5, reduction of uranyl(VI) in the presence of Fe(II) was discussed. Uranyl(VI) is known

to be reduced to U(IV) by Fe(II) in the presence of a certain ligand in solution or on a ferric (hydr)oxide surface. Without proper ligands and surfaces, the redox reaction such as $UO_2^{2+} + Fe^{2+} \rightarrow UO_2^+ + Fe^{3+}$ is endothermic. This is based on the simple estimate from reduction potentials for $UO_2^{2+}/UO_2^+$ of 0.088 V and for $Fe^{3+}/Fe^{2+}$ of 0.771 V. A certain type of ligands and surfaces make the reduction of uranyl(VI) by Fe(II) spontaneous. In this chapter, the possible reaction mechanisms facilitated by the presence of Fe(II)-containing systems were treated; (i) Succinic, malic, and tartaric acid are dicarboxylic acids with zero-, one-, and two-hydroxyl groups, the presence of which is known to facilitate the reduction of uranyl(VI) to U(IV) by Fe(II). These probably form ternary complexes with uranyl(VI) and Fe(II) which are linked by the dicarboxylates. It is assumed that the ternary complexes are intermediates in electron transfer from Fe(II) to U(VI), yielding finally U(IV). (ii) Dinuclear complex simply bridged by two hydroxides, $[U(VI)O_2(OH)_2Fe(II)](aq)^{2+}$, was used as a model of iron-containing minerals. Dinucler Fe cluster, $Fe(II)_2(OH)_4(H_2O)_6$, is also tested as a candidate for further extension of this approach. These relatively small clusters represent minimum models for edge- and corner-sharing configurations. Using small clusters is validated by the fact that electronic structures of metal centers, U(VI) and Fe(II), involved in electron transfer reactions are more important than the local adsorption structure on surfaces itself. In fact, it is known that the reduction of U(VI) occurs on iron-containing minerals, but the adsorption structures and redox mechanisms are still open questions. Some studies suggest that the redox reactions might occur in an amorphous phase of interface between mineral and water. In the above model reactions (i) and (ii), the only first half reduction processes, from U(VI) to U(V), were focused on because it is known that U(V) is shortly-lived in aqueous solution, and readily disproportionates to U(VI) and U(IV). This chapter proposed methods for investigation surface-catalyzed redox reactions and mentioned future prospective.


## 7. Conclusions

This study shows that DFT is successfully applicable to geochemistry on uranyl(VI): aqueous solution chemistry, redox, sorption, and coupling among them. Using proposed approaches can reproduce and predict reduction behavior of U(VI) in solution in the presence of solvation and ligand field effects. Modeling adsorption structures as a cluster can provide reliable geometry of surface complexes on a surface even in the presence of coexisting ligands. The proposed approaches offer future prospects for investigating a surface reduction of U(VI), and moreover geochemistry on transuranium elements.