

Thermochemical study of uranium by *ab initio* quantum chemical calculations

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Ab initio Hartree Fock (HF) theory and Density Functional theory (DFT) have been used to predict the Gibbs free energy of formation (ΔG_f^0) for uranium (VI) hydrolysis complexes. B3LYP is a better method to calculate the chemical properties of the complex and large molecules. The calculations were performed in the presence of solvent (water) by using the dielectric continuum modeling PCM method as well as the revised Born model. The pressure parameter $p=1354\text{atm}$ was used to reproduce the entropy of ions in solution. The calculated energy demonstrates that PCM model is better than Born model in calculating the hydration energy. The primary hydration shell has been included in the calculation. It shows that the B3LYP calculated results inclusive of the primary hydration shell and the PCM hydration energy have reasonable agreement with experiments.

Key words: Gibbs free energy, hydration energy, primary hydration shell, PCM model, revised Born model, uranium

1 Introduction

The understanding of interactions between spent nuclear fuel and intruding ground water, including hydrolysis products, is necessary to analyze the function and the safety of repositories for high-level radioactive waste (HLW). This requires prediction of the chemical behavior of the actinides. Knowledge about the chemical behavior of the actinides in aqueous media like groundwater systems is necessary to model the transport characteristics of these elements in the geosphere. Uranium is particularly important because of its relatively long decay period and relative abundance in nuclear waste. In the HLW repository, once the container fails, the nuclides like uranium will be released into the engineered barrier and transport through the geological environment, react with the groundwater and geological media, and finally arrive at the accessible human environment. The nuclides behavior study under the repository condition is very crucial. One of the most important chemical reactions of nuclides under repository is the hydrolysis of the nuclides. Study of the hydrolysis reaction of UO_2^{2+} can improve the understanding of actinyl hydrolysis reaction and more complex chemical phenomena in general.

The chemistry of uranium in aqueous media has caused considerable experimental interests[1-2]. One of them is its behavior at high temperature, high pressure and under reductive condition. However, it is quite difficult to obtain reliable experimental data under such condition due to the radioactivity of uranium and low solubility of uranium (IV) in neutral pH region. In this paper, quantum chemical calculations have been employed to study the hydrolysis of uranium (VI). It is an effective method to predict various properties of molecules and reactions, including molecular energies and structures, thermochemical properties, bond and reaction energies and so on. Therefore, we can combine the experimental data collected with theoretical results to predict the properties of those systems

that are difficult to access by experiments.

Since the actinide elements will react with water in geological media, solvent effect plays an important role in determining the chemical behavior of the actinides. Therefore, we must incorporate the solvent effects into the quantum chemical calculations of the solute molecules. The determination of the hydration energy of heavy atoms is very important. It is also a theoretical challenge to quantum chemical calculation. In the present paper, our main interest focuses on the hydration energy calculation. This work was intended as a first step towards developing theoretical methods for approximating the solubility of actinide oxides and hydroxides.

2 Theoretical Approach

The geometry optimization and energy calculation were carried out in the ideal gas phase using HF/6-311G**, MP2/6-311G** as well as the hybrid density functional method at B3LYP/6-311G** level. The optimized geometry was used in the subsequent solvation energy calculation. Spin-orbit effects were not considered here, since it is less important in the closed shell system that is considered here[3]. Effective core potential (ECP) and corresponding basis set were used for uranium[4]. Basis sets for oxygen and hydrogen were from Ref.[5]. All calculations were carried out using Gaussian 98 (Gaussian Inc.) suite of programs[6] except Table 1. For the calculation of

Table 1 The entropy of some uranium complexes

Uranium complexes	Calculated entropy (cal/mol•K)	Expt. entropy (in gas) (cal/mol•K)
UCl_3	90.83	90.82
UO_2	60.79	63.65
UF_6	94.85	89.99
UO_3	73.31	73.97
UF_2	72.09	75.53

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Table 2 The thermochemistries (kcal/mol) in ideal gas phase at $p=1\text{atm}$, $T=298.15\text{K}$

	Method	ΔE_{SCF} (kcal/mol)	ΔH^0 (kcal/mol)	ΔG^0 (kcal/mol)
(1-a) $\text{UO}_2^{2+}+2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^++\text{H}_3\text{O}^+$	HF	-129.18	-127.70	-120.33
(2) $\text{UO}_2^{2+}+4\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0+2\text{H}_3\text{O}^+$	HF	-107.89	-105.61	-87.14
(1-a) $\text{UO}_2^{2+}+2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^++\text{H}_3\text{O}^+$	MP2	-122.31	-126.19	-119.49
(2) $\text{UO}_2^{2+}+4\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0+2\text{H}_3\text{O}^+$	MP2	-98.21	-107.38	-89.17
(1-a) $\text{UO}_2^{2+}+2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^++\text{H}_3\text{O}^+$	B3LYP	-165.03	-163.35	-156.22
(2) $\text{UO}_2^{2+}+4\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0+2\text{H}_3\text{O}^+$	B3LYP	-154.32	-150.88	-132.98

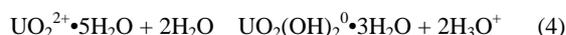
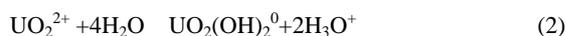
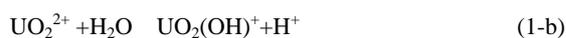
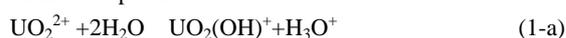
The first column is the theoretical method (the basis set is 6-311G**), the second column gives the electronic energy, the third column is the enthalpy, the fourth column is the Gibbs free energy.

Table1, quantum chemical calculation code Mulliken 2.0TM (IBM Corporation) was used at the HF level. 6-31G basis set in Mulliken 2.0TM was used for O[7], F[7] and Cl[8] atoms. ECP and corresponding double zeta basis set were used for uranium atom[9].

Hydration energy was calculated using continuum dielectric solvation modeling PCM(polarizable continuum model) method. During the liquid-phase calculations, a dielectric constant of $\epsilon=78.39$ was taken.

The hydration energy was also calculated using revised Born model[10]. The final total free energy in solution was calculated as the sum of the gas phase free energy and the hydration energy.

The following chemical reactions are calculated, which are the basis to understand other complex hydrolysis reactions of uranium. First, structure optimization was carried out, then the calculations of enthalpy and Gibbs free energy of the reactions were performed.



3 Results and Discussion

First, the entropy of some uranium complexes was calculated. The purpose is to obtain the general knowledge about the quantum chemical calculation in the gas phase.

Table 1 shows the calculated entropy of some uranium complexes at $T=298.15\text{K}$ and $p=1\text{atm}$. The calculated entropy has good agreement with the experimental entropy in gas phase. In other words, the calculated entropy is quite different from that in solution, and cannot be directly used to estimate the Gibbs free energy in solution. Because the Mulliken and the Gaussian programs consider the hypothetical ideal gas at concentration corresponding to the pressure $p=1\text{atm}$, the molecules have more freedom than they actually do in solution.

In order to obtain applicable results in liquid water, we use the pressure parameter $p=1354\text{atm}$, which corresponds to the density of water at $T=298.15\text{K}$, for the aqueous calculations[11]. This was done to reproduce the entropy of ions in solution.

We used HF/6-311G**, MP2/6-311G** and B3LYP/6-311G** methods to calculate the gas phase electronic energy, enthalpy and free energy. The results are presented in Table 2, while Table 3 adds the solvation contributions to the free energy. The optimized geometry in gas phase was used for the calculations of solvation energy. According to Li et al.[14] and Marcos et al.[15], the geometry of metal cations optimized in gas phase does not deviate much from those in solution phase.

The reaction Gibbs free energy change of reaction (1-a) as well as reaction (1-b) in solution using different methods was also presented in Table 3. The calculation of the free energy of proton H^+ is very difficult. According to previous calculation results[12,13], the best calculated Gibbs free energy of formation for H^+ is -260.5 kcal/mol . We use this value for the calculation of reaction energy of reaction (1-b).

The Gibbs free energy change of reaction (1-a) is quite different from reaction (1-b). The free energy change of reaction (1-a) is much closer to the experimental result[1] (as shown in Table 3). The main discrepancy probably comes from the energy of H^+ . Thus in the sequence calculation of reaction energy, we use H_3O^+ instead of H^+ , as shown in reactions (1) to (4).

It is seen from Table 2 and Table 3 that, for reaction (1-a) and reaction (2), the calculated electronic energy, enthalpy and Gibbs free energy changes are very close for HF method and MP2 method. The calculated energy at B3LYP level is somewhat smaller than those in HF and MP2 calculations even using the same basis set. The B3LYP method has been reported to underestimate the hydration energy for several types of reactions by other researchers[14,16,17].

It is shown from Table 3 that the free energy change of reactions in gas phase is quite different from that obtained by experiment. The hydration energy accounts for a large

Table 3 The thermochemistries (kcal/mol) in aqueous solution at $T=298.15\text{K}$

	Method	ΔG^0	ΔG	Born energy	ΔE_{PCM}	$\Delta G_{\text{aq}}^{\text{BORN}}$	$\Delta G_{\text{aq}}^{\text{PCM}}$	Expt.
(1-b) $\text{UO}_2^{2+} + \text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}^+$	HF	-209.78	-212.38	87.12	112.40	-125.26	-99.98	7.10
(1-a) $\text{UO}_2^{2+} + 2\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}_3\text{O}^+$	HF	-120.33	-116.17	87.12	118.22	-29.05	2.05	7.10
(2) $\text{UO}_2^{2+} + 4\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})_2^0 + 2\text{H}_3\text{O}^+$	HF	-87.14	-78.76	63.25	96.43	-15.51	17.67	14.10
(1-b) $\text{UO}_2^{2+} + \text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}^+$	MP2	-208.87	-211.09	87.08	109.79	-124.01	-101.30	7.10
(1-a) $\text{UO}_2^{2+} + 2\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}_3\text{O}^+$	MP2	-119.49	-115.19	87.08	116.37	-28.11	1.18	7.10
(2) $\text{UO}_2^{2+} + 4\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})_2^0 + 2\text{H}_3\text{O}^+$	MP2	-89.17	-78.47	73.66	92.32	-4.81	14.23	14.10
(1-b) $\text{UO}_2^{2+} + \text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}^+$	B3LYP	-246.74	-249.05	87.18	116.17	-161.87	-132.88	7.10
(1-a) $\text{UO}_2^{2+} + 2\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})^+ + \text{H}_3\text{O}^+$	B3LYP	-156.22	-152.16	87.18	122.19	-64.98	-29.97	7.10
(2) $\text{UO}_2^{2+} + 4\text{H}_2\text{O}$ $\text{UO}_2(\text{OH})_2^0 + 2\text{H}_3\text{O}^+$	B3LYP	-132.98	-121.10	58.97	96.52	-62.13	-26.58	14.10

The first column is the theoretical method (the basis set is 6-311G**), the second column is the gas phase free energy from Table 2, the third column is the free energy after adjustment for the concentration in the liquid ($p=1354\text{atm}$), the fourth column is the Born hydration energy, the fifth column is the PCM solvation free energy correction, the sixth column is the sum of the Born energy and the third column, the seventh column is the sum of the PCM solvation free energy and the third column. Experimental results are given in the final column. The unit is kcal/mol

proportion of the total energy of the solvation system. Thus, the determination of hydration energies is very important.

The hydration energy calculation results in Table 3 indicate that the PCM hydration energy has better agreement with the experimental result than the revised Born hydration free energy. We can conclude that the continuum dielectric theory PCM model provides a more reasonable means of calculating the hydration energies of molecules in water than

Born model.

There are several papers which discussed the Born model and they recommended the revised Born model[10,12-13,20-21]. According to Born model, it is clear that the accuracy of hydration energy critically depends on the radii of the molecules or ions. There are some papers that discussed the radius problem[9,19]. In our calculation, we use the cavity radius for the Born radius, and for cations and anions, the radii were increased by 0.85Å and 0.1Å, respectively. According to Li et al.[14] and Krauss et al.[19, 22], the Born equation results are too negative. We have the same conclusion. We think that another main discrepancy is from the neutral molecules. According to Born model the hydration energy of neutral molecules is zero. While for the PCM dielectric continuum solvation model the hydration free energy of neutral molecule is not zero, and sometimes as large as that of charged ions.

However, PCM dielectric continuum solvation model is also not the best model to calculate the hydration energy. First, the accuracy of PCM model depends on the effective scaling factor. According to Eugene et al.[23], the effective scaling factors for the neutral molecules are 1.20~1.25 and 1.10~1.15 for single charged ions. But for divalent or trivalent ions there are no suggested scaling factors. On the other hand, PCM model is also related to the atomic radii. The more reasonable atomic radii will give more accurate hydration energies.

According to Tsushima et al.[18], Martin et al.[11], and Li et al.[14], the calculations of metal ions in solution should be implemented inclusive of the primary (and secondary) hydration spheres, since the hydration waters themselves participate in reactions. So in the following calculations of UO_2^{2+} , the first hydration shell is included by using clusters like $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O}$, $\text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{OH})_2^0 \cdot 3\text{H}_2\text{O}$. We used B3LYP method, which is an effective compromise between accuracy and computational expense. 6-31G* basis set was used for optimization calculations, and 6-31++G** basis set for energy calculation to include the diffuse and polarization function for O and H. The optimized structures of $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O}$ and

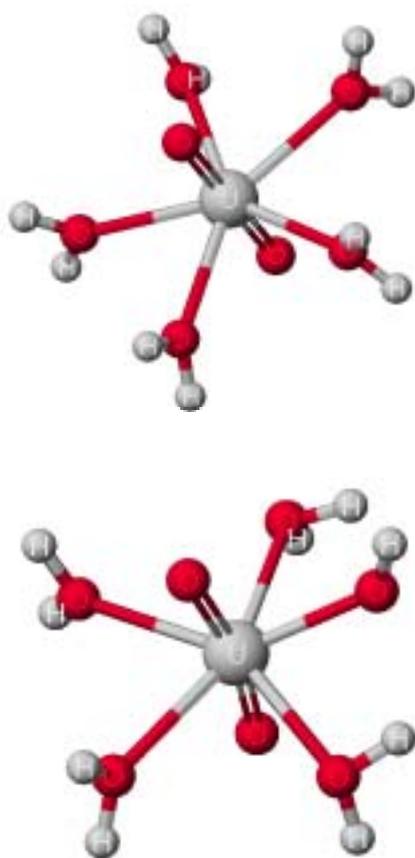


Figure 1 Optimized structure of $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O}$ (upper) and $\text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O}$ (lower)

Table 4 The thermochemistries (kcal/mol) in aqueous solution at T=298.15K at 6-31++G level**

	Method	ΔG^0	ΔG	ΔE_{PCM}	$\Delta G_{\text{aq}}^{\text{PCM}}$	Expt
(1-a) $\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^+ + \text{H}_3\text{O}^+$	B3LYP	-156.22	-152.16	122.19	-29.97	7.10
(2) $\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0 + 2\text{H}_3\text{O}^+$	B3LYP	-132.98	-121.10	96.52	-26.58	14.10
(3) $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O} + \text{H}_3\text{O}^+$	B3LYP	-25.00	-25.20	24.90	-0.30	7.10
(4) $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0 \cdot 3\text{H}_2\text{O} + 2\text{H}_3\text{O}^+$	B3LYP	25.6	25.3	-9.6	15.7	14.10
(3) $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O} + \text{H}_3\text{O}^+$	HF	-8.26	-8.29	23.16	14.87	7.10
(4) $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0 \cdot 3\text{H}_2\text{O} + 2\text{H}_3\text{O}^+$	HF	74.81	74.8	-33.09	41.71	14.10
(4) $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2^0 \cdot 3\text{H}_2\text{O} + 2\text{H}_3\text{O}^+$	MP2	59.77	59.36	-32.01	27.35	14.10

The first column is the gas phase free energy, the second column is the free energy after adjustment for the concentration in the liquid ($p=1354\text{atm}$), the third column is the PCM solvation free energy correction, the fourth column is the sum of the PCM solvation free energy and the second column, the fifth column is the experimental results. For reaction (3) and (4), the basis set for B3LYP and HF are 6-31G* for optimized calculation and 6-31++G** for energy calculation, while MP2 uses 6-31G* basis set for both optimization calculation and energy calculation. The unit is kcal/mol.

$\text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O}$ are shown in Figure 1. The reaction Gibbs free energies are reported in Table 4. The reaction (1-a) and (2) were also included in Table 4 for comparison. By comparing reaction (1-a) with reaction (3), reaction (2) with reaction (4), it is very clear that the absolute free energy of UO_2^{2+} calculated in solution with first hydration shell has better agreement with that obtained by experiment. According to Li. et al.[14], the inclusion of the secondary hydration shell substantially improves the accuracy of the thermochemical predictions, especially for highly charged cations. The participation of water molecules from the hydration shell in reaction is very crucial, because incorporation of water molecules into the hydration shell of UO_2^{2+} may get much closer to the practical situation in solution. It is not surprising that we can get more accurate results when we include the secondary hydration shell.

For the macroclusters $\text{UO}_2^{2+} \cdot 5\text{H}_2\text{O}$, $\text{UO}_2(\text{OH})^+ \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{OH})_2^0 \cdot 3\text{H}_2\text{O}$, the similar calculations were also conducted using HF method and MP2 method. The same basis set with B3LYP method was used for HF method. For MP2 method, 6-31G* basis set was used for both optimization calculation and energy calculation. The reason is that 6-31++G** basis set is too heavy for MP2 to carry out energy calculation because of the practical problem associated with the computation time. The reaction Gibbs free energies of (3) and (4) are shown in Table 4. It is interesting to find that the calculated Gibbs free energy using B3LYP method has the best accord to the experiment result than HF and MP2 method. It argues that the density functional method (B3LYP model) is an effective method to calculate the chemical properties of the complex and large molecules such as macroclusters of UO_2^{2+} ion, the correlation energy is better accounted in B3LYP than in MP2 method. In addition, MP2 method is very time consuming for large and complex molecules.

4 Conclusions

The reaction energy of hydrolysis reactions of UO_2^{2+} ion

was calculated using HF, MP2 and DFT methods. Hydration energy was included in the aqueous system. It is concluded that the calculated energy depends much on the quantum chemical calculation method and B3LYP method has the best accord to the experiment results. Inclusion of the first hydration shell improved the calculated energy. The dielectric continuum modeling PCM method is better than the revised Born model for the calculation of solvation energy, but still needs further improvement.

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References

- [1] Grenthe, I., Fuger, J., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H.: *NEA-TDB Chemical Thermodynamics of Uranium*, Nuclear Energy Agency, Organization for Economic Cooperation and Development, Elsevier Science, North-Holland, Amsterdam (1992).
- [2] Rai, D., Felmy, A. R., Ryan, J. L.: Uranium () hydrolysis constants and solubility product of $\text{UO}_2 \cdot x\text{H}_2\text{O}$. *Inorg. Chem.* **29**, 260-264 (1990).
- [3] Ismail, N., Heully, J. L., Saue, T., Daudey, J. P., Marsden, C. J.: Theoretical studies of the actinides: method calibration for the UO_2^{2+} ; and PuO_2^{2+} ions. *Chemical Physics Letters* **300** 296-302 (1999).
- [4] Ortiz, J. V., Hay, P. J., and Martin, R. L.: Role of d and f orbitals in the geometries of low-valent actinide compounds, *ab initio* studies of $\text{U}(\text{CH}_3)_3$, $\text{Np}(\text{CH}_3)_3$, $\text{Pu}(\text{CH}_3)_3$. *J.Am.Chem.Soc.* **114**, 2736-2737 (1992).
- [5] Krishnan, R., Binkley, J. S., Seeger, R. and Pople, K. A.: Self-consistent molecular orbital methods XX. A basis set for correlated wave functions. *J.Chem. Phys.* **72**, 650-654

- (1980).
- [6] Frisch, M. J, Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Peterson, G. A., Montgomery, J. A., Raghavachari, K., Allaham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cislowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., Pople, J. A.: *Gaussian 98 User's Reference*, (2nd edn.), Gaussian, Inc., Pittsburgh, PA (1998).
- [7] Hehre, W. J., Ditchfield, R., Pople, J. A.: Self-consistent molecular orbital methods.XII. further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **56**, 2257-2261 (1972).
- [8] Francl, M. M., Pietro, W. J., Hehre, W. J., Binkley, J. S., Gordon, M. S., Defress, D. J., Pople, J. A.: Self-consistent molecular orbital methods : A polarization-type basis set for second-row elements. *J. Chem. Phys.* **77**, 3654-3665 (1982).
- [9] Ermiler, W. C., Ross, R. B., Christiansen, P.A.: *ab initio* relativistic effective potentials with spin-orbit operators 6 Fr through Pu. *Int. J. Quantum Chem.* **40**, 829-846 (1991).
- [10] Rashin, A.A., Honig, B.: Revaluation of the Born model of ion hydration. *J. Phys. Chem.* **89**, 5588-5593 (1985).
- [11] Martin, R. L., Hay, J. P., Pratt, L. R.: Hydrolysis of ferric ion in water and conformational equilibrium. *J. Phys. Chem.* **102**, 3565-3573 (1998).
- [12] Tawa, G. J., Topol, I. A., Burt, S. K.: Calculation of the aqueous solvation free energy of the proton. *J. Chem. Phys.* **109**, 4852-4863 (1998).
- [13] Tossell, J. A.: Theoretical studies on aluminate and sodium aluminate species in models for aqueous solution: $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, and $\text{NaAl}(\text{OH})_4$, *American Mineralogist*, **84**, 1641-1649 (1999).
- [14] Li, J., Fisher, C. L., Chen, J. L., Bashford, D., Noodleman, L.: Calculation of redox potentials and pK_a values of hydrated transition metal cations by a combined density functional and continuum dielectric theory. *J. Inorg. Chem.* **35**, 4694-4702 (1996).
- [15] Marcos, E. S., Pappalardo, R. R., Rinaldi, D.: Effects of the solvent reaction field on the geometrical structures of hexahydrate metallic cations. *J. Phys. Chem.* **95**, 8928-8932 (1991).
- [16] Zhang Q., Bell, R., Truong, N.: *ab initio* and density functional theory studies of proton transfer reactions in multiple hydrogen bond systems. *J.Phys. Chem.* **99**, 592-599 (1995).
- [17] Durant, J. L.: Evaluation of transition state properties by density functional theory. *Chem. Phy. Lett.* **256**, 595-602 (1996).
- [18] Tsushima, S., Suzuki, A.: *ab initio* effective core potential study of equatorially coordinated uranyl species: effect of hydration to the calculated properties. *J. Mol. Struct.(Theochem)* **487**, 33-38 (1999).
- [19] Krauss, M., Stevens, W. J.: Analysis of protein metal binding selectivity in a cluster model. *J. Am. Chem. Soc.* **112**, 1460-1466 (1990).
- [20] Babu, S. C., Lim, C.: Theory of ionic hydration: insights from molecular dynamics simulations and experiment. *J.Phys.Chem.* **103**, 7958-7968 (1999).
- [21] Hu, C. H., Brinck, T.: Theoretical studies of the hydrolysis of the methyl phosphate anion. *J. Phys. Chem. A* **103**, 5379-5386 (1999).
- [22] Garmer, D. R., Krauss, M.: Metal Substitution and the active site of carbonic anhydrase. *J. Am. Chem. Soc.* **114**, 6487-6493 (1992).
- [23] Stefanovich, E. V., Truong, T.N.: Optimized atomic radii for quantum dielectric continuum solvation models. *Chem.Phys. Let.* **244**, 65-74 (1995).

