DFT Study on the U(IV)-PNPP Complex in Water

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1. Introduction

Since the toxicity of U(IV) has been considered as a potentially hazardous element in the environment, understanding U(IV) chemistry is important for the treatment of the nuclear waste.

Research has been focused on the fate of U(IV) in environmental chemistry in order to manage and remediate U-contaminated sites[1].

Therefore, the molecular level study on the structures and processes in the overall behavior of U(IV) has been investigated. Both experimental and theoretical studies have discussed complexation with various ligands[2]. However, para-Nitrophenylphosphate (PNPP) was not dealt with U(IV) in complexation study even though PNPP is one of the important substrates for phosphate binding chemistry at mineral-water interfaces and spectrophotometric biochemical assays[3].

Computational chemistry is a great complement to experimental studies of U(IV) chemistry because this methodology provides valuable information that is not available through the experiment, especially for transient materials and those with short kinetic times[4]. Herein, we performed the quantum calculation study on the complexation between U(IV) and PNPP to investigate several important chemical properties of the U(IV)-PNPP complex in water.

2. Quantum calculation on U(IV)-PNPP

2.1 Computation details

The B3LYP functional was utilized for geometry optimization at gas phase with tight energy and geometry convergence criteria without symmetry constraint. The ECP60MWB relativistic effective core potential and its associated basis set, which was developed by the Stuttgart-Cologne group, was chosen for describing Uranium and 6-31G(d) is used for P, N, O, C, and H. After the optimization, frequency calculation was performed and local minimum structure was confirmed by checking all positive frequencies. Those theoretical calculations were performed using Gaussian 09 packet.

2.2 Optimized Structures

Optimized structure of U(IV) ion in water was described with 8 and 9 water molecules (Fig. 1) [5]. Two water molecules of stable structures, $U(H_2O)_8^{4+}$(IV) and $U(H_2O)_9^{4+}$(IV), were exchanged by $PNPP^-$, respectively. Each complex was optimized in order to obtain the structure of U(IV)-PNPP complex in water. And then, the most stable spin state of the complex was found after calculating the energies of possible spin states (Fig. 2).

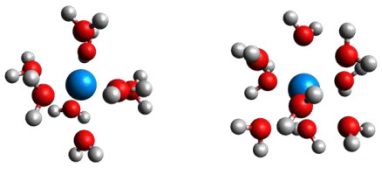

Fig. 1. Optimized structures of U(IV) ion in water.

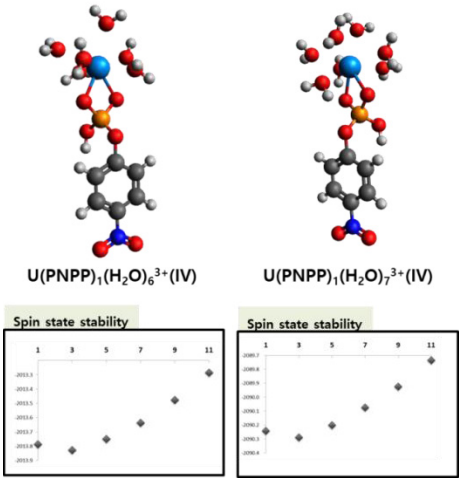

Fig. 2. Optimized structures of U(IV)-PNPP complex in water and energies of possible spin states in each complex.

2.3 Predicting Infrared Spectra

In each structure of U(IV)-PNPP complexes, Infrared spectrum was calculated by frequency calculation. And each complex shows the discernible signals (Fig. 3).

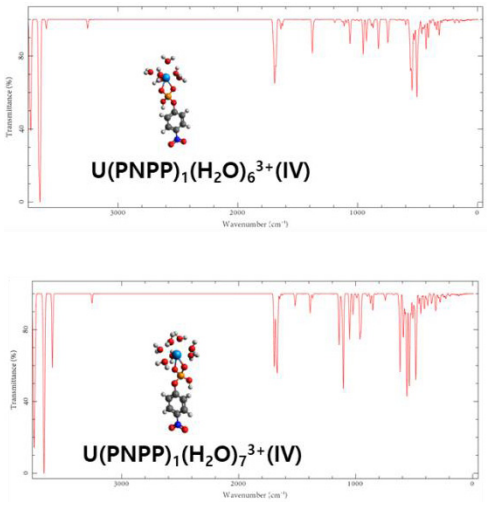

Fig. 3. Predicted infrared spectra for U(IV)-PNPP complexes in water.

3. Conclusion

Herein, we performed theoretical studies to obtain several important chemical properties of U(IV)-PNPP complex in water including their stable structures, spin state, and infrared spectra. This computational study may be a firm basis for the future applications on environmental researches of U(IV) and actinide chemistry in water.

4. Acknowledgment

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