Speciation and Binding of Uranyl Ion in Different Environments

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Abstract

Understanding the speciation and binding of heavy metal ions in different environments is central to nuclear waste management processes. Due to the obvious safety and health hazard in experimental studies, theoretical calculations can be used as an alternative tool to study the chemistry of toxic heavy metal ions. Although several quantum chemical methods with variable accuracy are available, a cost effective method such as density functional theory (DFT) is an obvious choice. Here, we have high-lightened some of our studies on the speciation of uranyl ion in aqueous, biological, geo-chemical, carbon based nanomaterials and with synthetic receptor environments.

Introduction

The chemistry of heavy metal ions such as actinyls is receiving increased attention at the present time due to the environmental danger posed by such species. In order to assess the extent of the hazardness, the speciation of toxic and heavy metal ions in various environments is at most essential.[1,2] As higher oxidation states of actinides such as uranyl ($U^{(VI)}O_2$) is toxic and soluble in water which is extremely dangerous for aquatic species. Thus viable strategies are needed which can convert toxic and soluble uranyl to non-toxic insoluble forms. One promising strategy is to make use of redox processes.[3]

Further, performing experiments on toxic heavy metal ions such as uranyl, chromate needs sophisticated laboratories which are generally very expensive. Further, some of the species involved in the conversion of $U^{(VI)}$ to $U^{(IV)}$ are usually very short lived intermediates such as $U^{(V)}$ and $Cr^{(V)}$ which are often not identified in experimental time scale due to the very short life time of the species. Alternatively, the speciation of heavy metal ions can be studied at the molecular level using molecular modeling methods.[4] In this regard, one can make use of cost effective molecular mechanics methods which can be used to study more than one million atoms, however, the accuracy is often questionable due to the parameters involved. Further, the electronic structure of the species under investigation can be studied with this classical method. The most accurate quantum chemical methods such as full Configuration Interaction methods (Full CI) with very large basis sets. Here too, due to the over-demanding computational cost even for a small system, some approximate methods are needed to study the chemistry of actinides. In this regard, methods such as CCSD(T) with triple ζ-basis set can now be regarded as affordable *ab initio* methods which can be considered as reference methods for single reference systems. If the system is truly multi-configurational, then methods such as Complete Active Space Self Consistent Field (CASSCF) should at least be used to treat the ground state degeneracy (often termed as static correlation), and the remaining dynamic correlation can be treated within the framework of MP2 methods. The most popular method is CASPT2 which can be even studied for systems of moderate sizes. [5]

Besides this, most of the heavy metal ions are often charged species such as tris-carbonate uranyl ($[UO_2(CO_3)_3]^{4-}$). Either, the species is highly solvated or exist in the presence of counter-ions. In addition to the methods chosen above, one need to take care of solvation as well. In this regard, either explicit solvation (treating each solvent molecule at the quantum chemical level) or implicit solvation such as polarizable continuum models are often used. Last but certainly not the least, to some extent relativistic and multiplet effect should be considered approximately. In this regard, scalar relativistic ZORA and DKH methods often predict results at least semi-quantitatively. [6] In fact, due to the large number of electrons in the heavy metal ions such as uranyl and the inner core electrons are often not involved in bonding, an effective core potential (ECP) is often used to model the inner core electrons. In this regard, a small core (SC) ECP is superior over large core ECP due to the better description of valence electron in SC-ECP.[4] It should be noted that some portion of relativistic effects are also incorporated in the ECPs which should predict ground state properties such as geometries and vibrational frequencies fairly well.

Our computational predictions on the speciation and binding of heavy metal ions in different environments are discussed in the next section. Due to the larger size of the systems involved, we have used BP86 density functional (DF) in conjunction with SC-ECP for core electrons and the valence electrons are described with double-ζ-basis set for geometry optimizations and triple-ζ-basis set for energetics. Solvent effects are incorporated within the COSMO solvation model.

Speciation of Actinyls in Aqueous Phase

The geometric and electronic structures of several small molecules directly bound to U, Np and Pu in both their (VI) and (V) oxidation states have been investigated using DFT methods. [7,8] Unlike the methods discussed above, we have accurately modeled the micro-solvation using molecular dynamics simulations and the bulk solvent using a continuum model. We find that two different hydrogen bonding patterns involving the axial actinyl oxygen atoms are sometimes possible, and may give rise to different An–O bond lengths and vibrational frequencies. These alternative structures are reflected in the experimental An–O bond lengths of the aqua and carbonato complexes (Fig. 1). The variation of the redox potential of the uranyl complexes with the different ligands have also been investigated.
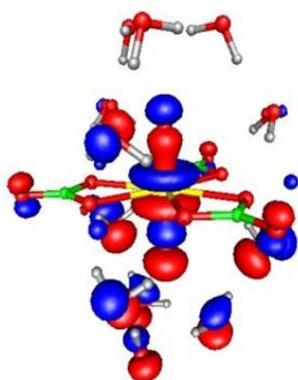

Fig. 1: Solvated structure of uranyl carbonate

Bio-reduction of Uranyl in Biological Systems

We have studied the possible binding, geometric structure and reduction mechanism of hydrated uranyl cation, $[UO_2]^{2+}$, to the electron transfer cytochrome c_7 protein.[9] Initially, the binding site of Uranyl to the protein is derived from AUTODOCK which is at glutamate and aspartate (Fig. 2). Further, the structures and reduction mechanisms are proposed based on DFT calculations. We proposed that the initial electron transfer takes place from the heme to a single uranyl ion.
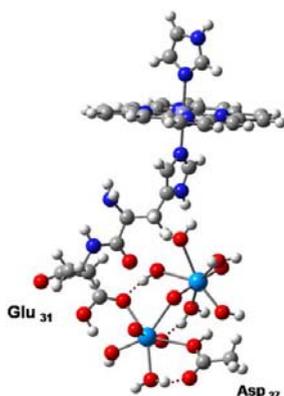

Fig. 2. T-shaped U-U dimer bound to protein

Further, a T-shaped cation-cation $U^{(V)}$-$U^{(VI)}$ complex with a second uranyl cation. A $U^{(V)}$-$U^{(V)}$ complex is formed, which then undergoes disproportionation via two successive protonation steps of one uranyl group, to give a $U^{(VI)}$-$U^{(IV)}$ complex which dissociates to individual $U^{(VI)}$ and $U^{(IV)}$ species, the former being bound at the enzyme active site. Intermediate structures along the catalytic pathway are consistent with the experimental data. A similar mechanistic pathways are also reported for chromate and for Pu and Np species. [10]

Speciation of Uranyl in Functionalized Carbon Nanotubes

One of the most commonly encountered problem in the back-end-of the nuclear fuel cycle is the selective binding of actinides in the presence of other interfering ions. Although many extractants are known, alternative viable extractants are explored. In this regard, we have investigated the use of carbon nanotubes and C_{60} fullerenes for the binding of uranyl. [11,12] Based on DFT calculations, we have shown that functionalized CNT can be used to bind uranyl ions much more efficiently as compared to their unfunctionalized counterpart. Further, we have also functionalized the CNT with supramolecule such as cucucurbituril (CB-[5]). We find that the binding of uranyl with CB-[5] upon bound to CNT is much stronger as compared to bare CB-[5] itself. [13] Recently, DFT based calculations on a series of uranyl complexes encapsulated with single walled (SW)-CNT to understand their encapsulation affinities (Fig. 3). We find that uranyl-aqua complex ($[UO_2(H_2O)_5]^{2+}$) binds stronger as compared to uranyl-hydroxo-complex ($[UO_2(OH)_4]^{2-}$) due to the variable overall charge of the complex. Further, we have considered the binding
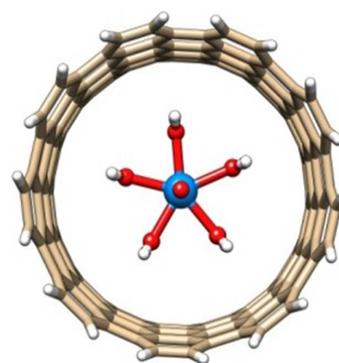

Fig. 3: Encapsulated hydrated uranyl to CNT

affinities of uranyl formate complexes with different formate stoichiometries (1:1, 1:2 and 1:3) with SW-CNT. [14] Here again, due to variable charges, cationic mono-formate-uranyl ($[UO_2(FM)(H_2O)_3]^{1+}$) complex binds stronger as compared to anionic tri-formate uranyl ($[UO_2(FM)_3]^{1-}$). Further, due to the very weak binding of commonly found in $[UO_2(FM)_3]^{1-}$ to CNT, we have sealed the tubular ends of SW-CNT with functionalized C_{36} fullerene. We note that binding affinity is not

improved as compared to its unsealed counterpart. However, upon functionalizing (at the hub carbon) the C_{36} cork, the binding affinity of $[UO_2(FM)_3]^{1-}$ is larger inside the CNT due to favorable hydrogen bonding interactions with the uranyl oxygens. Our findings are consistent with the recent experimental observations which will help to design novel nanomaterial for NWM processes.[15]

Selective binding of Uranyl with Novel ligands

Selective separation of uranyl ion from aqueous solution is one of the most important criteria for sustainable nuclear energy production. Very recently, we have investigated a known but unexplored extractant, tetraalkyl urea, which shows supreme selectivity (close to 100%) for uranium in the presence of interfering thorium and other lanthanide ions in nitric acid medium. [16] The structural characterization of the uranyl complex provides insight into stronger interaction between uranium and the ligand. The uranyl binding with the extractant is thermodynamically more favorable as compared to thorium and the selectivity is achieved through a combination of electronic and steric effects.

Speciation of Uranyl in Humic and Fulvic acid

The speciation of uranyl ion in fulvic acid (FA) and humic acid (HA), based on realistic models are systematically studied using density functional theory. [17] Due to the lack of crystal structure of availability of HA, a systematic way to attain the possible structure for HA is proposed based on a combined MD and quantum chemical approach. Our predicted geometric structure and energetics reveal many interesting features such as conformational flexibility computed for HA, in agreement with the experimental suggestions. Potential binding sites are proposed for uranyl binding to HA and FA. Our energetics reveals that apart from the uranyl carboxylate binding, additional binding sites such as chelation and hydroxo binding to uranyl should be considered as well.

Outlook

From the variety of systems that we have investigated, we believe that upon incorporating solvent effects and approximate relativistic effects within the DFT framework, we believe that quantum chemical calculations are extremely useful to understand the speciation and binding of heavy metal ions such as uranyl. Our computational strategy is a general strategy and thus can be used for other heavy metal ions such as cesium or amercium. [18-24]

Acknowledgements

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