Investigating the thermodynamics of the reduction of U(VI) to U(V) by Fe(II) using *ab initio* methods

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1   Background

During the nineties, the emphasis in my research group was on method development. We developed a new highly efficient method to calculate spin-orbit integral in the mean-field approximation, a new method to calculate spin-orbit effects using effective core potential (ECP) wave functions /1/ and developed an effective Hamiltonian formalism where high level correlation in are included in restricted spin-orbit configuration interaction (CI) calculations /2/. Our main quantum chemical tool has been the MOLCAS program package, developed by the theoretical chemistry group in Lund (with collaborators). Our programs were therefore with the general MOLCAS program package (see ref. 14 in Appendix 2). Later the project turned from method development to applications, largely in collaboration with professor emeritus Ingmar Grenthe at KTH. The applications have included structure and ligand exchange reactions in solution of uranyl, coordinated with water, fluorides, hydroxides, oxalates etc. /3–13/, redox reactions /14–17/ and gas phase reactions between six valued U, Np and Pu complexes such as MO_3, MF_6, MO_2F_2 and $MO_2(OH)_2$ /18, 19/.

2   Introduction

In the present work, we have addressed an important redox reaction, the reduction of U(VI) to U(V) in the presence of Fe(II). Redox reactions are not only of fundamental interest, to understand them is essential when describing how chemical reactions of actinides in surface and groundwater systems affect their mobility in the biosphere, and the function of engineered systems for the containment of radioactive waste in underground repositories. In this context it is important to notice that spent nuclear fuel is predominantly a matrix of UO_2 in which fission products and higher actinides are dispersed. In contact with water the fuel matrix will dissolve with a resulting release of the different radionuclides; the dissolution is a result of oxidation by radiolysis products or by intruding oxygen. In most technical system the nuclear waste is contained in canisters of iron/steel, which provide a large reduction capacity to the system and thus may prevent the transformation of sparingly soluble UO_2 to more soluble U(VI) species. Corrosion and other redox reactions involving iron species are therefore of key importance for the safe performance of many nuclear waste installations; as these have to function over very long time periods it is highly desirable to base predictions of their future environmental effects on molecular understanding of the chemical reactions taking place.

3   Results and Discussion

During the first phase of the project we investigated the thermodynamics of the reduction of U(VI) to U(V) by Fe(II) using *ab initio* methods. Our analyses are, in accordance with experimental information, based on the thermodynamics of the precursor and successor complexes formed before and after the electron transfer between uranium and iron. Experiments show that the rate of electron transfer is highly variable, but the detailed mechanisms of reactions involving actinides are very incompletely known. The overall stoichiometry of the reduction of U(VI) to U(V) by Fe(II) in water solution at different pH may be written as

$$UO_2(OH)_p^{2-p} + Fe(OH)_q^{2-q} \rightarrow UO_2(OH)_r^{1-r} + Fe(OH)_s^{3-s} \qquad (1)$$
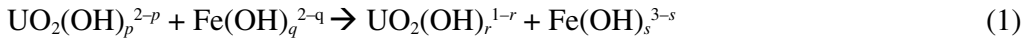
where $p + q = r + s = n = 4, 5, 6$, and the larger values of n present at higher pH. At low pH the first co-ordination shell consists mainly of water molecules that are replaced by hydroxide ions at higher pH. Equation (1) describes the stoichiometry of the redox reaction; the mechanism of the reaction is more complex (and largely unknown) and involves several steps. We explored an inner-sphere pathway involving two hydroxide bridges between iron(II) and uranium(VI) in the precursor complex and between iron(III) and uranium(V) in the successor complex. The latter is subsequently reduced to U(IV) and/or disproportionates according to

$$2U(V) \rightarrow U(IV) + U(VI) \qquad (2)$$

The over-all reduction of U(VI) to U(IV) by Fe(II) in solution is slow, presumably due to a slow reduction of U(V) to U(IV).

The focus of the study was on the reduction to U(V) as shown in equation 3.

$$[U(VI)O_2(OH)_pFe(II)]^{4-p} \rightarrow [U(V)O_2(OH)_pFe(III)]^{4-p} \qquad (3)$$
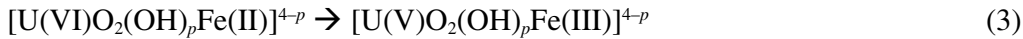
As this reaction involves the transfer of only one electron and minor rearrangements in the coordination spheres between U(VI) and U(V) we expect the reaction to be faster than the following reduction to U(IV). We have used different quantum chemical methods to determine the geometry and relative energy of different U(VI)/Fe(II) precursor and U(V)/Fe(III) successor complexes and the change in total energy during the reaction. U(VI) on the left hand side of reaction (3) is a closed shell system while Fe(II) has four open *d*-shells; on the right hand side of the reaction there is one open *f*-shell on U(V) and five open *d*-orbitals on Fe(III). We have assumed that the reduction of U(VI) and the simultaneous oxidation of Fe(II) take place through electron transfer from the iron *d*-shell into the empty 5*f*-shell of uranium, via bridging hydroxide ligands.

A general problem with actinides is the need to take the strong relativistic effects, the semi-core character of the 6*s* and 6*p* shells and the active role played by the 5*f*-orbitals, into account. The large number of electrons, which must be treated explicitly in the calculations, restricts the number of atoms, which can be included in the model. Another problem, specific for the present study, are the open *d*-shells on Fe(II) and Fe(III). The large number of both doubly occupied orbitals and unpaired electrons makes the calculations technically demanding, and in particular the correlation treatment becomes cumbersome. The net effect is that the calculations become very complicated. The reaction was studied in solution; solvent effects were included by the polarizable continuum model (PCM).

The U(VI)-Fe(II) and U(V)-Fe(III) complexes contain double hydroxide bridges, both in solution and in the gas phase. Experimentally the reaction is endothermic at low pH and exothermic at high pH.

According to our calculations the reaction is thermo-neutral or slightly exothermic for five and six hydroxide ligands, in agreement with observations, but exothermic with four hydroxides. The solvent effects were appreciable, of the order of 50 kJ/mol on the reaction energies in the case of four hydroxide ligands. The PCM model is, although often satisfactory, not a highly precise model, and the description of the solvent had to be improved. The complexity of the calculations only allowed us to add two extra water molecules to the four-hydroxide complex. As a result of this the PCM effect decreased to about 10 kJ/mol, and the results seemed more or less stable. We thus have good reasons to believe that the solvent effects, obtained with the PCM model, overestimate the reaction energy in particular in the four hydroxide complex, and that a better calculation would render the reaction endothermic. However, to add more water molecules to the complexes would make the calculations exceedingly difficult unless the computational model is simplified.

Our model is capable of reproducing experimental data reasonably well but it is not possible to improve the solvent model by adding more water molecules, or to apply it to cases with larger ligands such as carbonate. The results of this study have been published in J. Phys. Chem. A **107** 587–592 (2003) (Appendix 1, this report).

The main problem in this study was the description of the unpaired d-electrons on iron, and the simplification we chose was to develop a model for the iron ion where the problematic d-electrons were described by a simple potential. The approach has previously proved successful in models describing chemisorption and reactions on nickel and copper surfaces developed in our group. Dolg and co-workers have used a similar concept for the lanthanides, where ECPs which include the 4f-shell in the core have been quite successful /20/. The 3d-shell in Fe is more flexible than the 3d-shell in the transition metals to the right in the periodic table and the 4f-shell in the lanthanides, and more apt to participate in chemical bonds. However, the complexes of interest to us are highly ionic, with quite localized 3d-shells on Fe, and we deemed it worth the effort to develop a one-electron ECP also for Fe. Another complication in the present case is that we study redox processes, and it is unlikely that one single ECP can describe both Fe(II) and Fe(III). We thus decided to develop two different one-electron ECPs, one for Fe(II) and one for Fe(III). This would allow us to investigate for example solvent effects for the precursor and successor states (Fe(II) and Fe(III)) separately.

In the second phase of the project we developed very-large-core (one-electron) ECPs, which include the d-electrons in the core, for Fe(II) and Fe(III). The previous study of uranium reduction by Fe(II) provided data (geometries and relative energies of precursor/successor uranyl-iron complexes with different ligand arrangements) which could be used to optimize the model potentials. In addition to the U-Fe complexes the model has been applied to hydrated Fe(II) and Fe(III). We have also calculated geometries and relative energies in some iron-containing enzymes (the non-heme Fe(II)/Fe(III) phenylelanine hydroxylase).

Since different potentials had to be used for different oxidation states of Fe, it would at first sight seem as if the results cannot be used to calculate redox reaction energies. However, it turned out that a simple atomic correction gives excellent results for reaction energies obtained at the SCF level. The results were encouraging; both geometries and relative energies between conformers are reproduced at least on a semi-quantitative level. At the SCF level a correction factor which gives fairly accurate reaction energies can be obtained from atomic data, while at the MP2 level it seems necessary to use molecular data to deduce a correction factor. We are planning to pursue these studies in the future.

Geometries were reasonably well described in Fe(II)/Fe(III) phenylelanine hydroxylase, where the covalent interaction between the ligands and the metal is more pronounced than in the essentially ionic hydroxide complexes, while energy differences were less accurate. The approximation cannot be expected to work well for these systems where the d-orbitals participate directly in the bonding, but nevertheless we get reasonable geometries; in particular the topologies are correctly described which is an encouraging result. This study has been submitted for publication in J. Phys. Chem A (Appendix 2, this report).

4   Acknowledgement

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Reduction of Uranyl(VI) by Iron(II) in Solutions: An Ab Initio Study

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The reduction of uranyl U(VI) by Fe(II) in solution has been studied by quantum chemical methods, where the pH dependence of the reaction was simulated by using different numbers of coordinated hydroxide ions. The geometries for the binuclear U(VI)−Fe(II) precursor and the U(V)−Fe(III) successor complexes were optimized at the SCF level, and the reaction energies were calculated at the correlated level using the MP2 method. Effective core potentials were used throughout. Solvent effects were obtained by the polarizable continuum model. The accuracy of the solvent model was investigated for the binuclear complexes with two hydroxide bridges, and the accuracy of the MP2 method was assessed by comparing with CASPT2 and CCSD-(T) calculations on the smallest complexes. The general trends in geometry and reaction energy are consistent with experiment.

1. Introduction

The rapid development of both theory and software makes it possible to make detailed studies of the structure, thermodynamics, and reaction mechanisms of actinide complexes in gas phase and solution. Previous studies from our group and others indicate both the problems encountered and the level of detail in the chemical understanding that may be attained.[1-8] Chemical structures and the relative energy of different isomers may be predicted with high accuracy,[1,2] and it seems possible to obtain ab initio reaction energies for gas phase reactions that are in good agreement with experimental observations[3], even though the latter are often hampered by large errors. We have previously also studied ligand exchange mechanisms[4,5] using both experimental and theory-based activation enthalpies as a tool to identify the pathway of lowest activation energy. The present study is focused on redox reactions, an issue also addressed by us in previous studies.[6,7] These reactions are not only of fundamental interest; to understand them is essential when describing how chemical reactions of actinides in surface and groundwater systems affect their mobility in the biosphere and the function of engineered systems for the containment of radioactive waste in underground repositories. In this context, it is important to notice that spent nuclear fuel is predominantly a matrix of UO_2 in which fission products and higher actinides are dispersed. In contact with water, the fuel matrix will dissolve with a resulting release of the different radionuclides; the dissolution is a result of oxidation by radiolysis products or by intruding oxygen. In most technical systems, the nuclear waste is contained in canisters of iron/steel, which provide a large reduction capacity to the system and thus may prevent the transformation of sparingly soluble UO_2 to more soluble U(VI) species. Corrosion and other redox reactions involving iron

species are therefore of key importance for the safe performance of many nuclear waste installations; as these have to function over very long time periods, it is highly desirable to base predictions of their future environmental effects on molecular understanding of the chemical reactions taking place. Stumm and Sulzberger[8] have discussed the coupling between various geochemical processes and the Fe(II)−Fe(III) redox cycle, reactions often accelerated by surface sorption of reactants and products. Surface-catalyzed reduction of U(VI) by Fe(II) has been studied by Van Cappellen et al.[9] The catalytic action of Fe(III) in the U(IV)−U(VI) electron exchange in solution was studied by Tomiyasu and Fukutomi.[10] These reactions involve two one electron steps, where U(V) is present as an intermediate at very low concentration. The surface-mediated reactions involve the formation of surface complexes between iron and uranium; the electron exchange reactions in solution also involve specific inner sphere interactions between uranium and iron. It is well-known from experiments that Fe(II) does not reduce U(VI) to U(IV) at low pH, while the reaction is thermodynamically favored at high pH as a result of the formation of strong hydroxide complexes of U(IV) and Fe(III). These are in general polynuclear, containing hydroxide or oxide bridges known to be very efficient pathways for electron transfer between metal ions.[11-13]

In this paper, we will investigate the thermodynamics of the reduction of U(VI) to U(V) by Fe(II) using ab initio methods. The experimental data referred to above indicate that an analysis based on the thermodynamics of the precursor and successor complexes formed before and after the electron transfer between uranium and iron is a suitable first step in the analysis of the electron transfer mechanism. It is known from experiment that this rate is highly variable;[9,10,14] however, the detailed mechanisms of reactions involving actinides are very incompletely known. The overall stoichiometry of the reduction of U(VI) to U(V) by Fe(II) in water solution at different pH and low metal concentrations may be written as

$$UO_2(OH)_p^{2-p} + Fe(OH)_q^{2-q} \rightarrow UO_2(OH)_r^{1-r} + Fe(OH)_s^{3-s}$$

(1)

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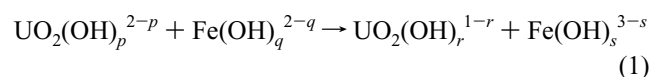
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where $p + q = r + s = n = 4, 5, 6$; the larger values of n are found at higher pH. At low pH, the first coordination shell consists mainly of water molecules that are replaced by hydroxide ions at higher pH. Equation 1 describes the stoichiometry of the redox reaction; the mechanism is more complex (and largely unknown) and involves several steps; we will explore an inner sphere pathway involving two hydroxide bridges between iron(II) and uranium(VI) in the precursor complex and between iron(III) and uranium(V) in the successor complex. The latter is subsequently reduced to U(IV) and/or disproportionates according to

$$2U(V) \rightarrow U(IV) + U(VI) \qquad (2)$$

The overall reduction of U(VI) to U(IV) by Fe(II) in solution is slow, presumably due to a slow reduction of U(V) to U(IV).

The reduction of U(VI) to U(V) as shown in eq 3 involves the transfer of only one electron and minor rearrangements in the coordination spheres between U(VI) and U(V); we expect the reaction to be faster than the following reduction to U(IV). We will use different quantum chemical methods to determine the geometry and relative energy of different U(VI)−Fe(II) precursor and U(V)−Fe(III) successor complexes and the change in total energy for reactions of the type

$$[U(VI)O_2(OH)_pFe(II)]^{4-p} \rightarrow [U(V)O_2(OH)_pFe(III)]^{4-p} \quad (3)$$
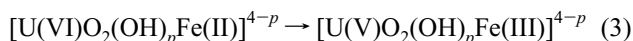
where U(VI) on the left-hand side of reaction 3 is a closed shell system while Fe(II) has four open d shells; on the right-hand side of the reaction, there is one open f shell on U(V) and five open d shells on Fe(III). In the model to be described, we assume that the reduction of U(VI) and the simultaneous oxidation of Fe(II) take place through electron transfer from the iron d shell into the empty 5f shell of uranium, via bridging hydroxide ligands.

The computation problem is very large and will require a number of approximations; the rationale for these will be discussed below. A general problem with actinides is the need to take the strong relativistic effects, the semicore character of the 6s and 6p shells and the active role played by the 5f orbitals, into account. The large number of electrons, which must be treated explicitly in the calculations, restricts the number of atoms that can be included in the model. Another problem, specific for the present study, are the open d shells on Fe(II) and Fe(III). The large number of both doubly occupied orbitals and unpaired electrons makes the calculations technically demanding, and in particular, the correlation treatment becomes cumbersome. The net effect is that it is exceedingly difficult to use a model with a complete first coordination shell.

Density functional theory (DFT)-based methods should in principle be technically well-suited for these systems. However, DFT calculations are very difficult in practice due to the electronic configurations of the precursor (four open d shells on iron(II)) and the successor (five open d shells on iron(II) and one open f shell on uranium(V)). Furthermore, as shown in ref 7, even the gradient-corrected DFT hybrid methods fail to describe the reduction of the uranyl(VI) ions properly.

2. Theory

2.1. Computational Model. Two factors have a strong influence on the choice of strategy for obtaining reliable energies and geometries; one is the problem of obtaining high quality correlation estimates and the other is the description of the solvent.

Correlation would ideally be obtained by some high level method such as CASPT2 or CCSD(T). The latter is precluded because of the size of the system. CASPT2 is in principle feasible, but ideally, the multireference CASPT2 calculations should be carried out with a large valence reference space, including excitations from the oxygen 2s, the uranium 6s and 6p, and, if applicable, 5f and iron 3d orbitals. However, the practical limit is around 16 electrons in 16 orbitals, a limit that is quickly reached, and a careful selection procedure must therefore be used to determine an optimal active space. The alternative is the simple, but for systems with a variable number of open shells, sometimes unreliable MP2 method. Our approach has been to assess its reliability by comparison with CASPT2 results on the smallest systems. This approach will be discussed further in the Results section.

The solvent effects were described using the polarizable continuum model (PCM)[15] as implemented in the Molcas[16] program package. We have considered complexes with 4−6 hydroxide ions in the precursor and successor complexes. Because of computational restrictions, we have not been able to saturate the first hydration shell with water molecules, as desirable when using the PCM model. Its accuracy when used without explicit coordinated water molecules was investigated by adding one or two additional water molecules in the calculations involving four hydroxides where the coordinative unsaturation is largest. For computational reasons, we also had to make symmetry restrictions on the geometry of the complexes.

The structures of the different complexes were optimized in the gas phase at the single reference SCF level using gradient technique with symmetry constraints. Energies in the gas phase and in the water solvent were obtained using the SCF optimized gas phase geometries. Although SCF optimized geometries in our experience are good for ionic actinide complexes, the internal uranyl bond is too short by approximately 0.06 Å at the SCF level.[7] However, this correlation effect on the bond length is similar when the oxidation state changes.[7] Furthermore, the SCF geometries give correct results for the reactions energies at the correlated level for gas phase reactions.[3]

2.2. Basis Sets. The program package Molcas5[16] was used throughout. Effective core potentials (ECP) of the Stuttgart type[17] were used for all atoms except hydrogen; previous studies[6,7] have proved their accuracy. The small core ECP with 32 electrons in the valence shell suggested in ref 18 was used for uranium. The oxygen atom was described by the same type of energy consistent ECPs,[19] but without polarizing d functions; for hydrogen, we used basis set parameters suggested by Huzinaga[20] with 5s functions contracted to 3s. The geometry optimizations were made using a hydrogen basis set without a diffuse p function, and the same basis set was used for the estimation of the correlation contribution to the total electronic energy. The reason for adopting the small basis sets was the severe convergence problems encountered when using extended basis sets with a d function on oxygen and a p function on hydrogen, rather than as a way to decrease the computation times. However, to estimate the accuracy of the calculations, we also made tests with extended basis sets (vide infra).

3. Results and Discussion

The redox reaction between U(VI)/U(V) and Fe(II)/Fe(III) occurs through electron transfer mediated by bridging oxide/hydroxide. The geometry and relative energy of the ground state structure of these binuclear intermediates will be discussed in this and the following sections. Unless explicitly stated, energies

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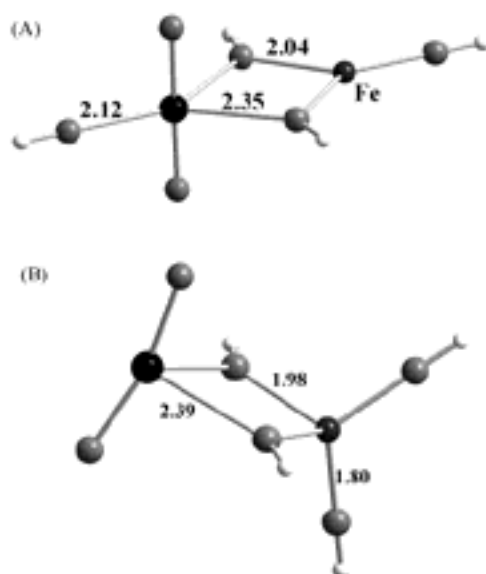
Figure 1. (A,B) SCF optimized ground state structure containing four hydroxide ions of U(VI)Fe(II) and U(V)Fe(III) precursor−successor complexes (see text). Bond lengths are shown in Ångstroms; see Tables S1,2 for details. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

quoted in the text have been obtained in the solvent employing the PCM model. They refer to the difference between the total energies of the successor and precursor complexes, and a negative reaction energy refers to an exothermic redox reaction.

3.1. Binuclear U−Fe Complexes Containing Four Hydroxide Ligands. *Ground States of the Precursor and Successor Complexes.* In the precursor complex, the two metal atoms are bound by two hydroxide bridges, with one additional hydroxide attached to uranium and iron, respectively (cf. Figure 1A). The most stable structure of the successor complexes also has a double hydroxide bridge, but in this case, the remaining two hydroxide ions are coordinated to Fe(III) (Figure 1B).

The ground state geometry of both the precursor and the successor complexes agrees with chemical expectations; U(VI) is a stronger acid than Fe(II) but not sufficiently strong to have four coordinated hydroxide ions. Fe(III) is a much stronger acid than U(V), and accordingly, the most stable structure has two terminal hydroxide ions on iron.

Alternative Structures. In addition to the ground state, we considered three precursor isomers of higher energy, one with a double bridge involving one hydroxide ion and one uranyl oxygen, 36 kJ/mol above the ground state (see Supporting Information), one with a double hydroxide bridge and both of the additional hydroxides attached to uranium, 65 kJ/mol above the ground state (see Supporting Information), and one with a double hydroxide bridge but with the two additional hydroxides attached to iron. This latter structure (see Supporting Information) is not stable in the solvent and has the highest energy in the gas phase of all isomers (208 kJ/mol above the ground state). For the successor complex, we also investigated three isomers with higher energy (see Supporting Information). The first one, 77 kJ/mol above the ground state, has two "yl" oxygen bridges and two hydroxide ions on each of U(V) and Fe(III). The second isomer with a mixed hydroxide/oxide bridge is 89 kJ/mol above the ground state, and the third isomer with a double hydroxide bridge and one additional hydroxide on each metal, as in the ground state for the precursor complex, is 119 kJ/mol above the ground state. We were surprised that isomers with bridges involving the yl ions were stable. However, there is experimental

TABLE 1: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four Hydroxide Ions (Ground State Geometries Are Considered)[a]

	SCF	CASSCF	MP2	CASPT2
gas phase	−10	155	27	42
PCM	−88	50	−16	−11

[a] A negative energy means that the reaction is exothermic.

evidence that they can be involved in coordination to other metal ions both in the solid state[21] and in aqueous solution.[22] The bond distances in the different structures are reasonably close to the values found experimentally in binary hydroxide complexes, indicating that the model approximations are satisfactory. The geometries and relative energies of four different precursor and successor complexes are given in Tables S1,2 in the Supporting Information.

Accuracy of the Correlation Treatment. The correlation contribution to the reaction energy is normally large in reactions where the number of open shells varies, and it is thus important that the correlation method used is satisfactory for the system under study. The easiest and most straightforward way to calculate the correlation contribution to the reaction energy is to use the MP2 method. In our case, the precursor has four open d shells on iron and the successor has five open d shells on iron and one open f shell on uranium. It is therefore necessary to assess the reliability of the MP2 method for this system. This was done in two different ways. First, CASPT2 calculations with an active space as large as we could afford and second, CCSD(T) and MP2 calculations on the naked ions UO_2^{2+}/UO_2^{+} and Fe^{2+}/Fe^{3+} in the gas phase.

The size of the complex with four hydroxides precludes a CASPT2 calculation in the full valence space including the oxygen 2s and 2p shells, and the calculations were therefore carried out in a restricted reference space. To determine the stability of the result, a sequence of calculations was carried out where the reference space was gradually increased. The result was assumed stable when the changes became 10 kJ/mol or less. Using this procedure, the CASPT2 results became stable, both in gas phase and in the solvent, with a CAS space generated by distributing 12 electrons in 11 orbitals for the precursor U(VI)−Fe(II) complex and 12 electrons in 12 orbitals in the successor U(V)−Fe(III) complex.

The calculated reaction energy for reaction 3 is shown in Table 1. The effect of correlation is large, both in the gas phase and in the solvent. The correlation effect is severely overestimated by the CAS calculation, which is not surprising since no dynamic correlation is accounted for (the contribution from dynamic correlation has usually the opposite sign as compared to that from static correlation). The agreement between the MP2 and the CASPT2 results is satisfactory; MP2 overestimates the correlation effect with 15 kJ/mol in the gas phase and 5 kJ/mol in the solvent. These results indicate that MP2 is a reasonable method to use for these systems.

As an additional test, we also carried out MP2 and CCSD-(T) calculations on UO_2^{+} and UO_2^{2+} and on Fe^{3+} and Fe^{2+} in the gas phase. The reaction energy for the reaction

$$UO_2^{2+} + Fe^{2+} \rightarrow UO_2^{+} + Fe^{3+} \qquad (4)$$
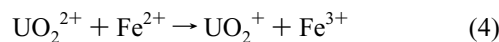
is 1541 kJ/mol at the MP2 level and 1511 kJ/mol at the CCSD-(T) level. MP2 thus overestimates the reaction energy with 30 kJ/mol relative to CCSD(T). This difference between the MP2 and the CCSD(T) results is acceptable.

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Redox Reaction. From the results in Table 1, it is seen that the correlation effect is larger for the U(VI)−Fe(II) than for the U(V)−Fe(III) system, as expected since the number of closed shells is larger in the former system than in the latter; correlation thus tends to make the reaction less favorable. The solvent effect works in the opposite direction, favoring the U(V)−Fe(III) complex. The solvent effect is of the same magnitude as that for correlation, about 50 kJ/mol (at the correlated level). It is a coincidence that the reaction energy obtained at the SCF level in the gas phase agrees with the correlated result in the solvent. The reason for the larger solvent effect for the U(V)−Fe(III) system is presumably its larger polarity as compared to the precursor. At the MP2 level, the reaction is exothermic by 16 kJ/mol (Table 1).

The electron transfer reaction in the 4 OH$^-$ system involves a structure change where one hydroxide moves from the uranium to the iron. In the solvent, this reorganization will probably be mediated by proton transfer reactions with the solvent. The change in the bond distances between the metal centers and the bridging hydroxides is moderate.

All structures were optimized with symmetry constraints, and the reaction energies might therefore change if the hydroxides are allowed to bend out of the equatorial plane. For example, for the UO$_2$(OH)$_4^{2-}$ complex in solution, the energy difference between a geometry where all of the hydroxide ions are constrained to the equatorial plane and the true minimum, which is a trans configuration with two hydroxide hydrogen atoms pointing upward and two downward, is 55.3 kJ/mol (the hydroxide oxygens are all close to the equatorial plane) or close to 14 kJ/mol for each hydroxide. However, from Figure 1, it is clear that the effect of allowing the hydroxides to bend out of the equatorial plane will be similar on the ground states of both the precursor and the successor complexes; hence, we do not expect that the symmetry constraint will result in a large error in the estimate of the reaction energy.

The U(VI)O$_2$(OH)$_4$Fe(II)·2H$_2$O Complex. The model with four hydroxide ligands and no coordinated water molecules leaves both the uranium and the iron centers coordinatively unsaturated. Therefore, the PCM model cannot be expected to describe the detailed interactions between the solvent molecules and the solute complex with a high accuracy. It is therefore desirable to saturate the first hydration shell before using this model, but this was not possible in our case. To estimate the error caused by an incomplete first coordination sphere when using the PCM model, we have added one or two water molecules to the precursor and successor complexes. These calculations could only be made on the structures with a high symmetry, otherwise they become prohibitively large; for the precursor, we used the isomer with both hydroxides coordinated to uranium, 65 kJ/mol above the ground state (Figure S3, Supporting Information). The information obtained from this investigation is used to estimate the errors in the solvent model when using an incomplete coordination shell, assuming that the solvent effect is approximately the same for all isomers. The bond distances of the hydrated complexes are given in Table S5 of the Supporting Information.

The reaction energies are shown in Table 2. At the SCF level, the reaction energy in the solvent decreases from −151 kJ/mol for the four hydroxide complex to −104 kJ/mol with one added water molecule and to −81 kJ/mol with two added water molecules. The solvation effect at the SCF level decreases from 25 kJ/mol for no water, to 5 kJ/mol for one water, to 4 kJ/mol for two water molecules. At the MP2 level, the reaction energies in the solvent are −67, −13, and −19 kJ/mol, and the solvation

TABLE 2: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four Hydroxide Ions and No. 1 and 2 Water Molecules[a]

	no H$_2$O SCF	no H$_2$O MP2	one H$_2$O SCF	one H$_2$O MP2	two H$_2$O SCF	two H$_2$O MP2
gas phase	−176	−118	−109	−43	−77	−23
in solvent	−153	−67	−104	−13	−81	−19

[a] A negative energy means that the reaction is exothermic. The precursor has a double hydroxide bridge and two hydroxides attached to uranium. For the complex with no added water molecules, this isomer is 65 kJ/mol above ground state (see text).
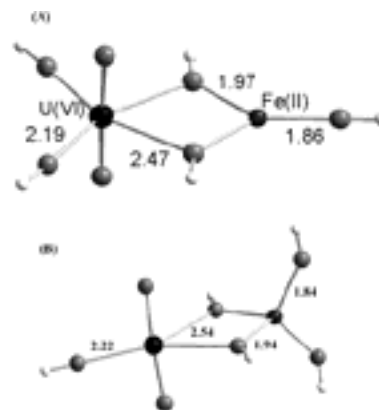
Figure 2. SCF optimized geometry of precursor (A) and successor (B) complexes with five OH groups. Bond distances are in Ångstroms. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

effect is 51, 30, and 4 kJ/mol. These results show that already one water molecule has an appreciable effect and that two water molecules essentially mimic the saturation of the first coordination shell of both iron and uranyl.

Two conclusions concerning the PCM model may be drawn from these results. First, the reaction energy obtained for the four hydroxide complex is overestimated. Second, precursor/successor complexes with five ligands (including the bridging hydroxides) provide a reasonable description of the solvent effects, and six ligands mimic the saturation of the first coordination shells of both metal ions.

3.2. Binuclear U−Fe Complexes Containing Five and Six Hydroxide Ligands. For the complexes with five and in particular six coordinated hydroxide groups, a new difficulty is that the electronic ground states in gas phase and in the solvent were different for the successor complex; the open 5f shell on uranium changed character from (5f−6d) to a pure 5f in solution. The effect on the geometry of a change in the character of the open 5f shell should be minor due to the localized character of this orbital. We have therefore used the gas phase geometries (see Figures 2 and 3) to obtain reaction energies in the solvent. However, the reaction energies in the gas phase and in solution can no longer be compared, and we therefore restrict the discussion to the reaction energies in solution.

Electronically, precursor/successor complexes with four, five, and six hydroxides are very similar. We are therefore confident that MP2 is reliable also for the five and six hydroxide complexes. In the previous section, we showed that the computed solvent effects are described in a satisfactory way with five and six coordinated ligands.

A summary of the reaction energies for the complexes with four, five, and six hydroxide ligands is given in Table 3 (the bond distances of the five and six hydroxide complexes are

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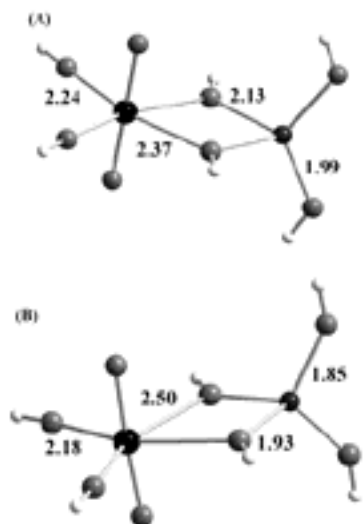
Figure 3. SCF optimized geometry of precursor (A) and successor (B) complexes with six OH groups. Bond distances are in Ångstroms. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

TABLE 3: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four, Five, and Six Hydroxide Ions in the Solvent[a]

complex	SCF	MP2
four hydroxides	−88	−16
five hydroxides	−67	−13
six hydroxides	−57	−23

[a] A negative energy means that the reaction is exothermic.

given in Tables S6 and S7 in the Supporting Information). The reaction is exothermic for all complexes. However, our investigation of the solvent effect showed that the reaction energy is overestimated in the unsaturated four hydroxide complex and that the reaction would probably turn out to be endothermic with a better solvation model. The reaction energy for the precursor−successor reaction for the six coordinated hydroxides (the equilibrium constant for $UO_2(OH)_2^-$ has been assumed to be the same as for $NpO_2(OH)_2^-$), −23 kJ/mol, is close to the experimental value for the Gibbs energy of reaction for reaction 1, about −20 kJ/mol,[23] but this agreement is fortuitous.

4. Estimation of Basis Set Errors and Spin−Orbit Effects

The calculations have been done using a rather small basis set without polarizing functions on O and H. To investigate how sensitive the results are to the size of the basis set, we recalculated the geometry and total energy for the complex with four hydroxides with one d function on oxygen and one p function on hydrogen added to the basis set.

A larger basis set introduced new computational difficulties. At the MP2 level, the calculations for the U(V)−Fe(III) complexes became unstable due to large contribution of configurations with small denominators in the perturbation expansion. The problem is similar to that with intruders in excited state calculations. A well-tested method to eliminate the problem of small denominators is to use the level shift technique proposed in ref 24. A level shift of 0.1 Hartrees makes the MP2 results stable for the successor complex. To compare the energies of the precursor and the successor complexes, we have to use the same level shift for both systems. When we use this procedure, the reaction energy changes from 16 kJ/mol (exothermic) to 26 kJ/mol (endothermic). The energy change remains almost the same with further increase of the level shift

up to 0.5 Hartrees. From these results, we conclude that the large basis set stabilizes the precursor complex by about 40 kJ/mol relative to the successor complex.

Spin−orbit effects will stabilize Fe(II) relative to Fe(III), since the atomic ground state for the latter, ^6S, is not split by spin−orbit effects, while the U(V) will be stabilized relative to the closed shell U(VI) system. The spin−orbit effect in Fe(II), estimated from the experimental atomic fine structure, is about 8 kJ/mol, while a calculation on UO_2^+ gave a spin−orbit effect of 25 kJ/mol. The latter result is consistent with the spin−orbit effect on the reduction of UO_2^{2+} to $UO(OH)^+$ reported in ref 6. The spin−orbit effect will thus stabilize the U(V)−Fe(III) complex by 15−20 kJ/mol.

An increased basis set and the spin−orbit effects give opposite contributions to the total energy. The net result indicates a slight stabilization of the precursor complex by about 20 kJ/mol. Our best estimate is thus that the reaction for the four hydroxide complex is slightly endothermic while the reactions for the five and six hydroxide complexes are close to thermoneutral (endothermic by 7 kJ/mol and exothermic by −3 kJ/mol, respectively). This is in fair agreement with the experimental observations.[23]

5. Conclusions

The U(VI)−Fe(II) and U(V)−Fe(III) complexes contain double hydroxide bridges both in solution and in the gas phase. Experimentally, the reaction is endothermic at low pH and exothermic at high pH. According to our calculations, the reaction is thermoneutral or slightly exothermic for five and six hydroxide ligands. We have good reasons to believe that the solvent effects, obtained with the PCM model, overestimate the reaction energy in the four hydroxide complex and that a better calculation would render the reaction endothermic. Such a calculation would be very difficult unless the computational model is simplified. At the present level of accuracy, our results are consistent with experimental observations. The theoretical U(V)−Fe(III) and U(VI)−Fe(II) distances are comparable with the experimental U(VI)−Fe(III) distances of uranyl(VI) ions sorbed on the Fe(III)-containing minerals (see ref 24 for details).

Our model is consistent with experimental data, but it is not possible to improve the solvent model by adding more water molecules or to apply it to cases with larger ligands such as carbonate. We are investigating the possibility to simplify the model by a more approximate treatment of the Fe(II) and Fe(III) ions, and the results are promising. This will be the subject of a forthcoming paper.

Supporting Information Available: Figures S1−S3 and Tables S1−S7 showing the structures of precursor and successor complexes with, respectively, 4−6 coordinated hydroxide ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Reduction of uranyl(VI) by iron(II): application of a new Effective Core Potential for Fe(II) and Fe(III)

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Abstract

In a previous article we studied the reduction of UO_2^{2+} by Fe^{2+} in solution at the *ab-initio* level, using conventional small core Effective Core Potentials of the Stuttgart type. The calculations were difficult due to the large number of open shells on Fe. In the present paper we present very-large-core Effective Core Potentials where the d-electrons are included in the core for Fe(II) and Fe(III). Our purpose is to develop a method which may be used for qualitative or semi-quantitative studies of the ionic iron-complexes without the limitations created by a large number of unpaired d-electrons. Obviously, we expect the best performance for a d-electron model potential in complexes without a strong involvement of d-electrons in bond formation.

The new ECPs are primarily designed to describe ionic uranium complexes such as the uranium-iron complexes bound by bridging hydroxide ions of interest in the reduction reaction. The new ECP works well for the bridged complexes and for hydrated Fe(II) and Fe(III) complexes, and reasonably well for geometry optimization of suitable organo-metallic complexes.

Introduction

It is accepted notion that in most chemical processes the core electrons produce little more than a constant potential for the valence electrons. Therefore a natural approximation is to describe the effect of the core electrons by means of a fixed potential, thus limiting the computational effort to an explicit description of only the valence electrons. The method is known as the effective core potential (ECP) or model potential (MP) method. The size of the core used in the calculations is a matter of choice and varies between different ECPs. The accuracy of small core MP and ECP methods, where the outer core electrons such as 3s and 3p for the first row transition metals normally are included in the valence, has been thoroughly tested and found accurate at all levels of theory. The obvious advantage of employing the MP is the reduction of computational costs for the extended systems and systems containing heavy elements.

In a recent communication[1] we have reported a study of the reduction of uranium(VI) by iron(II) in solution, as a part of a project with the objective to improve the understanding of the chemical

reactions in canisters for long term storage of nuclear waste[2]. However, since both Fe(II) in the precursor state, and U(V) and Fe(III) in the successor state contain a number of open shells, the calculations became cumbersome. The technical problems associated with the open shells are both problems to identify proper ground states, and related convergence difficulties, and long computational times with the hardware and software at our disposal. Indeed, it became unfeasible to carry out calculations with more than six light ligands (hydroxide ions in our case), or less if the symmetry restrictions are lifted. This was particularly disturbing since solvent effects turned out to be important and in some instances probably poorly described within the continuum model.

In a previous model used to describe chemisorption and reactions on nickel and copper surfaces, a "very-large-core" ECP was developed where the metal atoms were described by the 4s electron only, and the 3d shell was included in the core[3]. This surface model was successful in reproducing properties such as geometries and binding energies of an adsorbate[3,4]. Dolg and co-workers have used a similar concept for the lanthanides, where ECPs which include the 4f-shell in the core have been quite successful[5]. The 3d-shell in Fe is more flexible than the 3d-shell in the transition metals to the right in the periodic table and the 4f-shell in the lanthanides, and more apt to participate in chemical bonds. However, the complexes of interest to us are highly ionic, with quite localized 3d-shells on Fe, and we deemed it worth the effort to develop a very-large-core ECP, in the following abbreviated VLC-ECP, also for Fe. Another complication in the present case is that we study redox processes, and one single ECP can not describe both Fe(II) and Fe(III). We thus decided to develop two different VLC-ECPs, one for Fe(II) and one for Fe(III). This would allow us to investigate for example solvent effects for the precursor and successor states (Fe(II) and Fe(III)) separately.

The previous study of uranium reduction by Fe(II)[1] provides data (geometries and relative energies of precursor/successor uranyl-iron complexes with different ligand arrangements), part of which we have used to optimize the VLC-ECPs. We have also calculated geometries and relative energies for hydrated Fe(II) and Fe(III), also used in the calibration procedure, and for (a model of) the non-heme Fe(II)/Fe(III) phenylelanine hydroxylase enzyme.

Since different VLC-ECPs have to be used for different oxidation states of Fe, it would at first sight seem as if the results cannot be used to calculate redox reaction energies. However, it turns out that a simple atomic correction gives excellent results for reaction energies obtained at the SCF level. At the correlated level a simple atomic correction did not yield acceptable results, due to important correlation effects in the d-shell.

Theory

The ECP method and the parametrization procedure we use have been outlined in detail in Ref 3 and 4. In this section we give only short overview of the very-large-core ECP formalism.

The starting point is the parametrization of the ECP Hamiltonian in the following form:

$$H^{eff} = T + U^{eff} + P \tag{1}$$

where T is the usual kinetic energy operator and U^{eff} is the potential energy operator. In the MP formalism the potential energy operator reads

$$U^{eff} = -\frac{Z^{eff}}{r}[1 + \sum_p A_p \cdot e^{-\alpha_p r^2} + \sum_q r B_q \cdot e^{-\beta_q r^2}] \tag{2}$$

Here Z^{eff} refers to the screened nuclear charge. The first sum describes primarily the corrections for the incomplete screening of the nuclear charge. Evidently the parameters A_p, α_p and B_q, β_q are optimized such U^{eff} corrects for other effects such as exchange interactions between core and valence and the effects of basis set reduction. The first term in the level-shift operator

$$P = \sum_c |\psi^c > C_c < \psi^c | + |\zeta > \lambda < \zeta | \qquad (3)$$

accounts for core-valence orthogonality effects and prevents the collapse of the valence orbitals on the core region. The second term is a correction term used to modify the Pauli interaction with neighboring atoms. The first term is constructed from the atomic core orbitals ψ^c, while ζ in the second term is an auxiliary Gaussian function.

In the present model the core consists of the 1s, 2s, 2p and 3d orbitals. The reason for keeping the 3s and 3p orbital in the valence is purely technical, and contribute little to the computational cost (see ref 3 and 4 and references therein). Formally, 9 electrons are thus included in the valence space, but since essentially only the 4s electron contribute to the chemical bonds the ECP is still effectively of the one-electron ECP type[3,4]. The last term in Equation (3) is intended to modify the interaction between the atomic d-functions and neighboring atoms, and ζ is consequently a primitive d-type Gaussian function.

The summation in the first sum in Equation (3) runs over the core orbitals (including the 3d orbital). The C_k parameters are put equal to or somewhat larger than the absolute value of the orbital energy of the corresponding core orbital ψ^c, in the case of Fe 1s, 2s, and 2p. ζ has d symmetry, and the parameter λ and the exponent of ζ are optimized together with the C_{3d} parameter to mimic the geometries and binding energies obtained for known molecular systems, in the present case the complexes with four hydroxide ions studied in reference 1, and, for refinement, Fe(II) and Fe(III) coordinated with 2, 4 and 6 water molecules. For details of the procedure see see Ref. 3 and 4 and references therein.

Technical details

The ECP parameters, including C_{3d}, λ and the exponent of the ζ, function, were optimized to reproduce results from all-electron calculations as described in the previous section. The ECP used to describe the Fe(II) ion was optimized for the singly charged Fe ion with the electron configuration $1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^2\ 3d^6\ 4s^1$, and similarly the ECP used to describe the Fe(III) ion was optimized for the doubly charged Fe ion with the electron configuration $1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^2\ 3d^5\ 4s^1$.

The all electron wave function for iron was obtained using an uncontracted 16s-, 12p-, 9d- and 4f basis set[6]. The basis set used in the ECP calculations consisted of 6 primitive s-functions and 8 primitive p-functions contracted to 3 s and 2 p. The orbital exponents in the ECP basis were obtained from a least squares fit to the orbital shape of the all electron 3s, 4s and 3p atomic orbitals. The ECP basis sets can be found in Supplementary information, contraction data.

In the totally symmetric part of the ECP, Equation (2), only the screening term (the first term in Equation (2)) was used. The parameters A_p, α_p were optimized to reproduce the all electron 3s, 3p and 4s orbital energies of the appropriate Fe ion. The Fe(II) and the Fe(III) ECPs reproduced the 3s-, 4s-, and 3p- orbital energies with the errors 0.0825, 0.0202 and .02269eV and 0.0947, 0.0072 and 0.081eV respectively. Parameters of the model potential are presented in Tables S1 and S2.

Effective Core Potentials (ECP) of the Stuttgart type[7] were used for uranium and oxygen; previous studies[8,9] have proved their accuracy. The small core ECP with 32 electrons in the valence shell suggested in Ref.10 was used for uranium. The oxygen atom was described by the same type of energy consistent ECP's[11], but without polarizing d-functions, for hydrogen we used basis set parameters suggested by Huzinaga[12] with $5s$ functions contracted to $3s$.

Solvent effects were described using the Polarizable Continuum Model (PCM)[13] as implemented in the Molcas[14] program package. The structures of the different complexes were optimized in the gas phase at the single reference SCF level using gradient technique with symmetry constraints. Energies in the gas phase and in the water solvent were obtained using the corresponding SCF optimized geometries

The program package Molcas5[14] was used throughout.

Results

In this section we compare results obtained with our VLC-ECP and with standard small-core Stuttgart type ECPs[7] (referred to below as *ab initio*).

Ionization Potentials.

Table 1 summarizes SCF results for the ionization potentials.

The agreement is good, although the VLC-ECP somewhat overestimates the ionization potential. The largest error, 0.5 eV, occur for the $3d^6\,4s^2 \rightarrow 3d^6\,4s^1$ ionization using the Fe(II) ECP. The reason for this error in unclear to us. The errors in the remaining IPs are small, below 0.1 eV.

The uranium-iron complexes

The complexes with four hydroxides are depicted in Fig. 1 and Fig. 2 for the precursor and successor complexes respectively. Fig. 3, 4 and 5 show the complexes with 4 hydroxides and two coordinated water molecules, 5 hydroxides and 6 hydroxides.

The Fe-U distances, the bond distances to the bridging oxygens and the relative energies for the U(VI)-Fe(II) complexes are shown in Table 2. The Fe-U distance is in all reproduced within 0.07 Å by the VLC- ECP, and the Fe-O$_{bridge}$ distances are all within 0.04-0.09 Å compared to the *ab-initio* results. The relative energies of the complexes are reproduced to within 20 kJ/mol.

Table 3 shows the corresponding results for the U(V)-Fe(III) complexes. The errors in the bond distances are somewhat smaller: within 0.03-0.07Å range. The complex with one hydroxide group and one uranyl oxygen is reproduced decently (Fig. 2b). How ever, the relative energy of the complex with both uranyl oxygen atoms in the bridging position (Fig. 2a) is less satisfactorily described by the VLC-ECP, presumably because of a stronger interaction between the iron and oxygen cores and polarization of the d-orbitals in the iron ion.

The Fe(II)/Fe(III) complexes with four OH groups were used for the optimization of the ECP parameters, and the verification of the model is thus given by the results obtained for the 5OH, 6OH and 4OH+2waters complexes. The bond distances and angles between the *ab initio* structures and ECP results are well reproduced by the ECP for the latter complexes.

Redox reaction energies

Since different ECPs are used to describe the Fe(II) and the Fe(III) ions reaction energies for the redox reaction U(VI)/Fe(II) →U(V)/Fe(III) cannot be calculated directly. However, the ECPs describe the binding situation well for the Fe(II) and the Fe(III) complexes, and if the reaction energy can be separated into contributions from the ligand-metal interaction and an essentially atomic contribution, then the difference between the total ECP energies of the Fe(II) and the Fe(III) ions (which has no relation to the actual IP since the ECPs are different) can be used to correct the calculated reaction energy. The idea is the following. The total energy difference between Fe(II) and Fe(III) obtained with the one electron ECPs contains two contributions: the actual ionization potential and a factor which is entirely due to differences in the ECPs. This latter factor, which is the desired correction, can then be calculated as the difference between the total energy of the Fe(II) and Fe(III) ions calculated with the ECPs, and the IP calculated at the all-electron level. The correction factor thus obtained is large, 6.11991104 a.u., but it should be kept in mind that this factor has no physical significance, it only reflects the differences in parameters for the two ECPs.

Redox reaction energies obtained at the *ab initio* level and using the VLC-ECPs with the atomic correction factor are shown in table 4.

The agreement is surprisingly good, the error compared to the *ab initio* results is in general below 15 kJ/mol.

The solvent effects are, as pointed out in ref. 1, large, in particular for the complexes with four and five hydroxide ligands, while it is much smaller for four hydroxides and two water molecules, and reasonably small for six hydroxides. This is probably due to the larger geometrical differences between the precursor and the successor for the four- and five hydroxide systems.

In the gas phase, at the SCF level, the five hydroxide complex behaves quite differently from he others. The reaction is endothermic by 19 kJ/mol, while the other complexes all are exothermic. The differences decreases in the solvent, where the largest effect, 100 kJ/mol, occur for the five hydroxide complex (cf Table 4). As mentioned in rex xx, the character of the open f-shell in the successor complex is different in gas phase and in the solvent, and the fact that the ground state changes character in the solvent explains both the difference between the five hydroxide complex and the other complexes, and the large solvent effect obtained for the five hydroxide complex.

At the MP2 level the situation is very different. The atomic correction gave very large errors, and it seems that the correlation contribution to the reaction energy no longer can be separated into atomic and ligand contributions. The reason behind this may be that the "atomic" correlation contribution

is strongly affected by interactions between the d-orbitals and the ligands. If this is the case a correction factor cannot be obtained from atomic data. As a less attractive alternative, we instead calculated a correction factor based on the four hydroxide complex. The results are shown in table 5.

The results are of similar quality as those obtained with the atomic correction at the SCF level. However, the procedure is not entirely satisfactory, since we have to use one of the complexes under study for the correction term, but the results indicate that an approach involving some correction factor may be used to obtain reasonable reaction energies. We have not pursued this question further in the present study, and the correction obtained from the four hydroxide complex can be used in our planned study of solvent effects.

Other possibilities would be to use for example hydrated Fe(II) and (III) for the purpose. We have not investigated such possibilities, since in the present context the procedures suggested in this study are appropriate for our purposes.

Iron-water complexes

Table 6 shows results with 2, 4 and 6 coordinated water molecules for Fe(II) and for Fe(III).
The VLC-ECP overestimates the Fe-O bond length both for Fe(II) and for Fe(III). The error decreases monotonically with an increased number of coordinated water molecules, from 0.08 to 0.04 Å for the Fe(II) complex and from 0.06 to 0.04 Å for the Fe(III) complex for 2 and 6 coordinated waters. The error in the binding energy per water molecule shows a similar trend; it decreases from 35 kJ/mol to 22 kJ/mol to 13 kJ/mol for the Fe(II) complexes and from 29 kJ/mol to 18 kJ/mol to 13 kJ/mol for the Fe(III) complexes as the number of coordinated water molecules is increased. The observed trends are expected since the bonds are getting longer, and the model thus more appropriate, as the number of coordinated water molecules is increased.

The errors obtained for the hydrated Fe ions are of the same order as those obtained for the U-Fe complexes. The hydrated complexes were used in the parameter optimization process and the results do thus not serve as a verification of the model. However, the overall agreement for all the U-Fe and hydrated iron complexes provides a strong indication that the model can be applied in cases where the bonds are largely ionic (or electrostatic) and the bond distances are reasonably long. In particular, the results strongly suggest that the VLC-ECPs can be used for example to investigate hydration effects by adding more water molecules, or in models of iron oxide surfaces.

The model of the non-heme Fe(II)/Fe(III) phenylalanine hydroxylase enzyme

Our final test is optimization of the structures of a model of the non-heme inron complex located at the active site of the phenylalanine hydroxylase (PAH) enzyme, shown in fig. 6.

Fe(II) phenylalanine hydroxylase has previously has been studied by Siegbahn et al[16]. The iron, in the second oxidation state, is bound to histidine and glutamatic acid, which in the model used were replaced with two imidazole rings and formate (HCOO⁻). The iron is six coordinated in the resting complex, and the total charge of the model complex is +1. It is believed that the ligands generate a weak field which stabilizes the high spin state of iron(II). The ab initio calculations were carried out at the unrestricted HF level with the 6-31G basis sets using Gaussian98[15]

The VLC-ECPs work quite well for the ionic systems tested so far, but we would not expect a comparable accuracy for the enzyme, where the d-orbitals are expected to play a much more active role. However, the geometries obtained with the VLC-ECP are surprisingly good. The error in the bond distances was below 0.05Å for the bond from iron ion to the nitrogen atoms in the imidazole rings. The errors were larger for the bonds to the water molecules, 0.14-0.38 Å, but the conformation of the complex remained very similar to the *ab initio* structure. As an additional test we optimized the structure of the complex where we substituted iron(II) by iron (III). The geometries were quite satisfactory: the error in the bonds from iron(III) to nitrogen atoms in the imidazole rings were less than 0.06Å and the errors in the iron-water bond distances decreased to below 0.05Å and

However, the energies obtained at the SCF level were less satisfactory. The energy difference between the Fe(II) and the Fe(III) complexes, obtained with the atomic correction described in a previous section, which is of the order of 800 kJ/mol (calculated at the SCF level) is overestimated by more than 100 kJ/mol by the ECP. The failure of the atomic correction is probably due to the strong interaction between the ligand orbitals and the d-orbitals on the iron. A similar situation occurred at the MP2 level for the hydroxide complexes.

Conclusion

In the present study we present a new very-large-core ECP for Fe(II) and Fe(III) of the "one-electron" type[3,4], with the 3d shell included in the core. This type of ECPs are known to perform well in cluster models of first row transition metals to the right in the periodic table, and for the 4f elements in the lanthanide series.

The results are encouraging; both geometries and relative energies between conformers are reproduced at least on a semi-quantative level. Furthermore, we have suggested a correction procedure which makes it possible to use very-large-core ECPs also to calculate redox reaction energies. At the SCF level a correction factor which gives reaction energies at a semi-quantitative level can be obtained from atomic data, while at the MP2 level it seems necessary to use molecular data to deduce a correction factor.

The suggested very-large-core ECP is useful for ionic Fe complexes and long Fe-ligand bond lengths. However, there are many instances where this situation is at hand, in particular in inorganic chemistry. The method can also be used for example for cluster models of oxides or other surfaces.

Although geometries seems to be reasonably well described in organic systems with a more pronounced covalent interaction between the ligands and the metal, energy differences were less well described.

Acknowledgements

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Tables

Table1. Ionization potentials (in eV) of iron ions and atom. The *ab initio* results are obtained with the small core Stuttgart ECP. Values in the brackets are the deviation between our very-large-core (VLC) ECP results and IPs calculated with the Stuttgart- type small-core ECPs (referred to as *ab initio* in the table)

Ionization	VLC-ECP	Present results	*ab initio*
$3d^6\ 4s^2 \rightarrow 3d^6\ 4s^1$	Fe(II)	6.95 [0.5]	6.43
$3d^6\ 4s^1 \rightarrow 3d^6\ 4s^0$	Fe(II)	15.44 [0.02]	15.42
$3d^5\ 4s^1 \rightarrow 3d^5\ 4s^0$	Fe(III)	25.95 [0.0.06]	25.89
$3d^5\ 4s^2 \rightarrow 3d^5\ 4s^1$	Fe(III)	15.73 [0.09]	15.64

Table.2. Calculated structure and relative stability of the dinuclear U(VI)-Fe(II) precursor complexes. The distances are in Å and energy is in kJ/mol. *ab initio* refer to results obtained with the Stuttgart- type small-core ECPs. Numbers in [] refer to the bond angles. VLC-ECP stands for the very-large-core ECP developed in this study.

Complex	U-Fe VLC-ECP	Fe-O$_{bridge}$ [angle]	Energy, VLC-ECP	U-Fe *ab initio*	Fe-O$_{bridge}$ [angle]	Energy, *Ab initio*
4OH, ground state	3.43	2.12 [84.4]	0 (g.s.)	3.42	2.04 [84.5]	0 (g.s.)
4OH, Fig. 1a	3.38	2.11/2.21 [73.9]	22	3.31	2.04/2.11 [74.7]	21
4OH, Fig 1b	3.39	1.92 [99.60]	150	3.36	1.85 [104.7]	166
4OH, Fig 1c	3.36	2.50 [73.6]	221	3.40	2.43 [76.8]	208
4OH and 2H$_2$O, Fig. 3	3.46	1.99 [91.1]	-	3.53	1.96 [85.2]	-
5OH, Fig. 4	3.55	2.04 [84.8]	-	3.53	1.97 [85.3]	-
6OH, Fig. 5	3.68	2.22 [76.6]	-	3.62	2.30 [77.5]	-

Table.3 Calculated structure and relative stability of the dinuclear U(V)-Fe(III) precursor structures. The distances are in Å and energy is in kJ/mol. *ab initio* refer to results obtained with the Stuttgart- type small-core ECPs. Numbers in [] refer toi the bond angles. VLC-ECP stands for the very-large-core ECP developed in this study.

Complex	U-Fe VLC-ECP	Fe-O$_{bridge}$ [angle]	Energy, VLC-ECP	U-Fe *ab initio*	Fe-O$_{bridge}$ [angle]	Energy, *Ab initio*
4OH, ground state	3.50	2.01 [83.1]	0	3.47	1.98 [83.8]	0
4OH, Fig. 2a	3.20	1.97 [82.2]	79	3.11	2.04 [76.1]	10
4OH,Fig 2b	3.37	1.85 /1.99 [88.1]	70.0	3.31	1.78 1.901 [87.7]	61
4OH, Fig 2c	3.48	1.88) [98.71]	150.3	3.49	1.83 [99.7]	141
4OH and 2H$_2$O, Fig 3	3.54	1.99 [93.6]	-	3.51	1.92 [95.0]	-
5OH, Fig. 4	3.54	1.98 [88.7]	-	3.52	1.94 [89.1]	-
6OH, Fig 5	3.58	1.96 [84.2]	-	3.55	1.92503 [84.9]	-

Table.4. Reaction energies for the U(VI)-Fe(II) →U(V)-Fe(III) reaction at the SCF level in gas phase and in a solvent (using the PCM model). *ab initio* stands for calculations with the explicit treatment of d-electrons with standard Stuttgart-type small core ECP as implemented in MOLCAS5. Energies are in kJ/mol, negative energy corresponds to the exothermic reaction. The atomic correction described in the text has been used. Numbers in () refer to the difference between Solvent and gas phase energies for ECP *and ab initio* calculations.

Complex	Gas phase, VLC-ECP	In solvent, VLC-ECP (solvent effect)	Gas phase, *ab initio*	In solvent, *ab initio* (solvent effect)
4OH	-25	-92 (-67)	-10	-88 (-78)
4OH, 2H$_2$O	-92	-84 (+8)	-77	-81 (+4)
6OH	-84	-48 (+36)	-67	-56 (11)
5OH	19	-81 (100)	4	-67 (71)

Table.5. Reaction energies for the U(VI)-Fe(II) →U(V)-Fe(III) reaction at the MP2 level in gas phase and in a solvent (using the PCM model). *ab initio* stands for calculations with the explicit treatment of d-electrons with standard Stuttgart-type small core ECP as implemented in MOLCAS5. Energies are in kJ/mol, negative energy corresponds to the exothermic reaction. A correction obtained from the 4 hydroxide complex described in the text has been used, and consequently there are no entries in the table for this complex. Numbers in () refer to the difference between solvent and gas phase energies for ECP *and ab initio* calculations. VLC-ECP stands for the very-large-core ECP developed in this study.

Complex	Gas phase, VLC-ECP	In solvent, VLC-ECP, (solven effect)	Gas phase, *ab initio*	In solvent, *ab initio,* (solvent effect)
4OH, 2H$_2$O	-35	-7.1 (+27.9)	-23	-20 (+3)
6OH	18	-5.4 (-23.4)	42	-13 (-55)
5OH	-99	-15 (+84)	-109	-23 (+86)

Table6. Comparison of very-large-core ECP and *ab-initio* (Stuttgart-type small-core ECP) calculations for the aqueous complexes of iron (III)/ iron (II) at the SCF level. Distances are given in Å and energies in kJ/mol. Values in parentheses are the deviations of the model potential geometry. The distances in the table are average values.

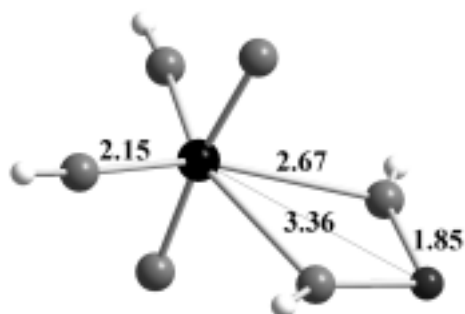| Complex	Fe-water Distance, Å	Error in binding energy per water molecule (kJ/mol)
Fe(III)+2H$_2$O	1.95 [0.06]	29
Fe(III)+4H$_2$O	2.05 [0.05]	18
Fe(III)+6H$_2$O	2.11 [0.04]	13
Fe(II)+2H$_2$O	2.02[0.082]	35
Fe(II)+4H$_2$O	2.13 [0.065]	22
Fe(II)+6H$_2$O	2.31 [0.041]	13

Figures
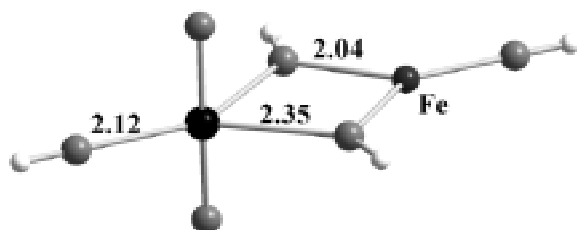
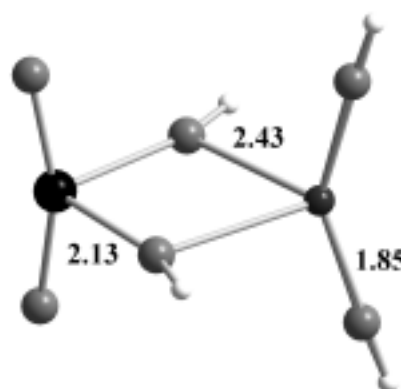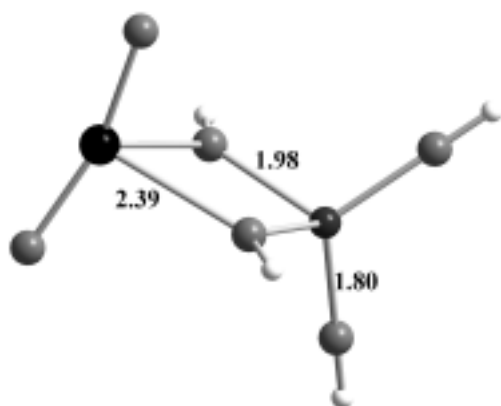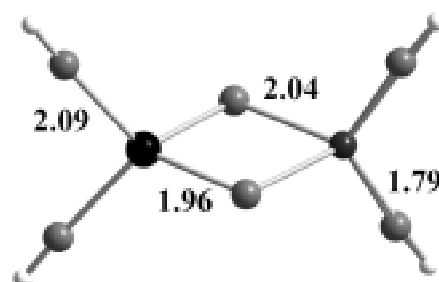**Ground state**   (a)
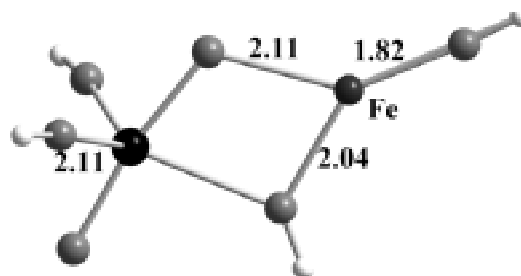
(b)   (c)

Fig 1. Ground state and four higher isomers a,b,c of the precursor U(VI)-Fe(II) complex. Distances are in Å optimized at the all-electron level. The U(VI) is on the left hand side and Fe(II) on the right hand side of the complex.
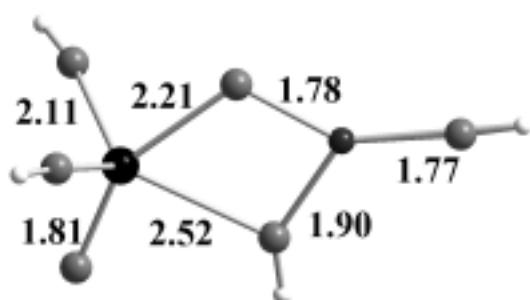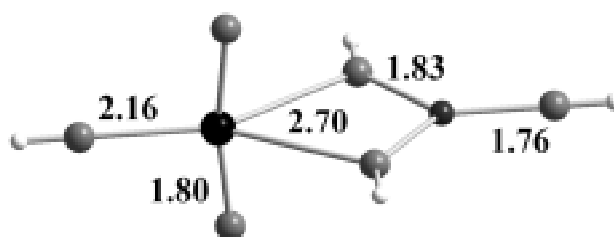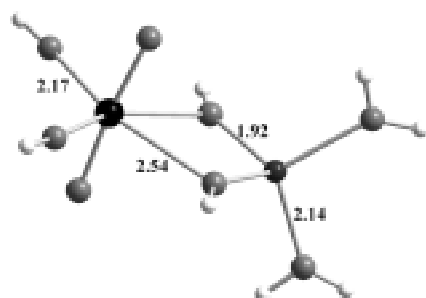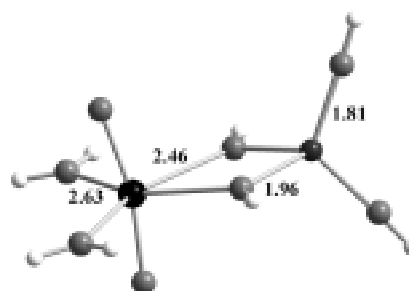
Ground state　　　　　　　　　　　　　　　　**(a)**

(b)　　　　　　　　　　　　　　　　**(c)**

Fig 2. Ground state and four higher isomers a,b,c of the successor U(V)-Fe(III) complex. Distances are in Å optimized at the all-electron level. The U(V) is on the left hand side and Fe(III) on the right hand side of the complex.

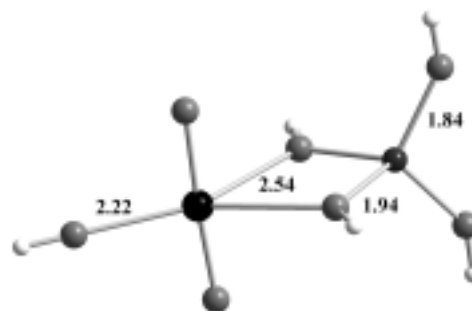**Precursor**   **Successor**

Fig. 3. SCF optimized geometry of precursor (a) and successor (b) complexes with four OH groups and two additional water molecules. Bond distances are in Å (see detailed information in Table S5. The U(VI)/U(V) is on the left hand side and Fe(II)/Fe(III) on the right hand side of the precursor/ successor complexes

Precursor   **Successor**
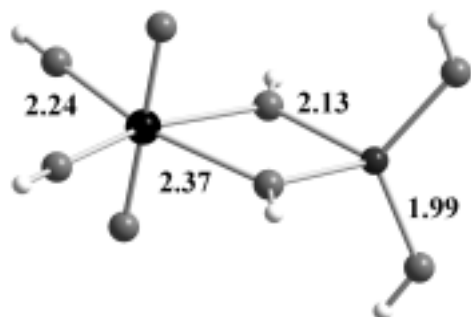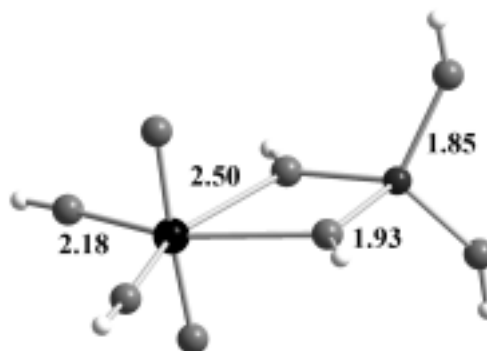

Fig.4. SCF optimized geometry of precursor and successor complexes with five OH groups. Bond distances are in Å. The U(VI)/U(V) is on the left hand side and Fe(II)/Fe(III) on the right hand side of the precursor/ successor complexes
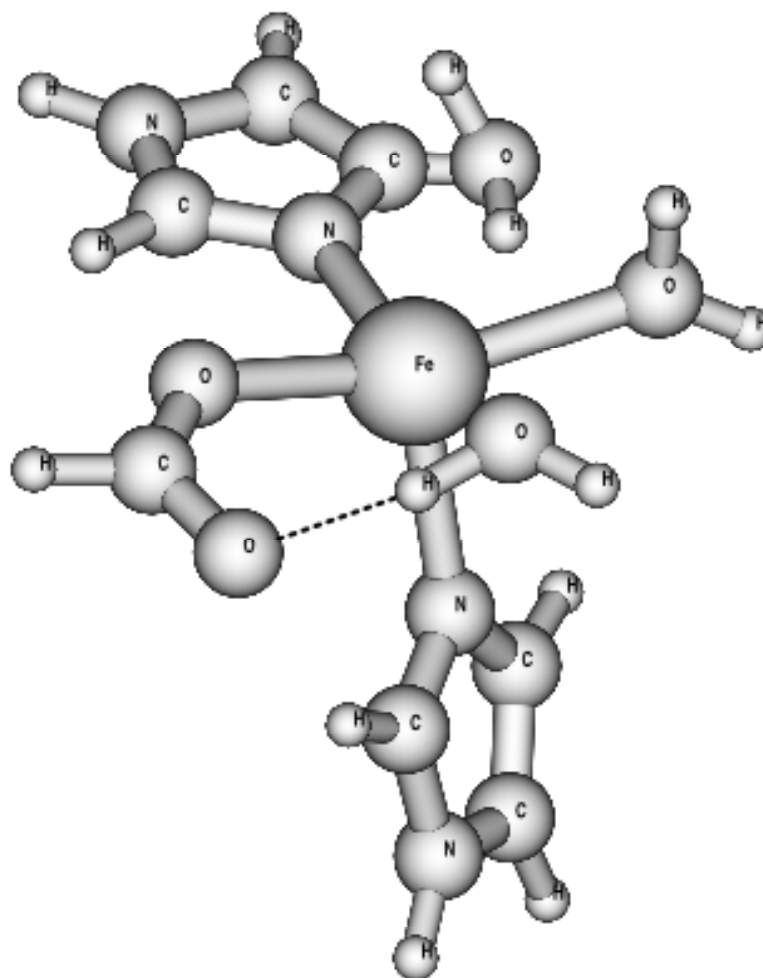
Precursor   **Successor**

Fig.5 SCF optimized geometry of precursor and successor complexes with six OH groups. Bond distances are in Å. The U(VI)/U(V) is on the left hand side and Fe(II)/Fe(III) on the right hand side of the precursor/ successor complexes.

Fig. 6. The model of the Fe(II) phenylalanine hydroxylase enzyme. The geometry shown in the picture was obtained with the present ECP.