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Electron Transfer in Neptunyl(VI)−Neptunyl(V) Complexes in Solution

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The rates and mechanisms of the electron self-exchange between Np(V) and Np(VI) in solution have been studied with quantum chemical methods and compared with previous results for the U(V)−U(VI) pair. Both outer-sphere and inner-sphere mechanisms have been investigated, the former for the aqua ions, the latter for binuclear complexes containing hydroxide, fluoride, and carbonate as bridging ligand. Solvent effects were calculated using the Marcus equation for the outer-sphere reactions and using a nonequilibrium PCM method for the inner-sphere reactions. The nonequilibrium PCM appeared to overestimate the solvent effect for the outer-sphere reactions. The calculated rate constant for the self-exchange reaction $NpO_2^{+}(aq) + NpO_2^{2+}(aq) \rightleftharpoons NpO_2^{2+}(aq) + NpO_2^{+}(aq)$, at 25 °C is $k = 67\ M^{-1}\ s^{-1}$, in fair agreement with the observed rates 0.0063−15 $M^{-1}\ s^{-1}$. The differences between the Np(V)−Np(VI) and the U(V)−U(VI) pairs are minor.

1. Introduction

In a previous article we have investigated the electron self-exchange between U(V) and U(VI),[1] and in the present study this has been extended to the electron transfer between the corresponding neptunium species.

Available information on the rates and mechanisms of electron exchange reactions of the early actinides has been reviewed in 1975 by Newton[2] and in 1982 by Tomiashu et al.[3] The most recent studies are to our knowledge Howes et al. from 1988,[4] and our own theoretical study from 2004.[1]

The rate and mechanism of four different electron self-exchange reactions, for which $\Delta G° = 0$, were studied using different chemical/quantum chemical models:

$$NpO_2^{+}(aq) + NpO_2^{2+}(aq) \rightleftharpoons NpO_2^{2+}(aq) + NpO_2^{+}(aq) \tag{1}$$

$$Np^{V}O_2(OH)_2Np^{VI}O_2 \rightleftharpoons Np^{VI}O_2(OH)_2Np^{V}O_2 \tag{2}$$

$$Np^{V}O_2F_2Np^{VI}O_2 \rightleftharpoons Np^{VI}O_2F_2Np^{V}O_2 \tag{3}$$

$$Np^{V}O_2(CO_3)Np^{VI}O_2 \rightleftharpoons Np^{VI}O_2(CO_3)Np^{V}O_2 \tag{4}$$

For reaction 1 we can make comparison with experimental data for the isotope exchange reaction between Np(V) and Np(VI)

$${}^{*}NpO_2^{+}(aq) + NpO_2^{2+}(aq) \rightleftharpoons {}^{*}NpO_2^{2+}(aq) + NpO_2^{+}(aq) \tag{5}$$

from Cohen et al.[5a,b]

As in ref 1, the rate for reaction 1 was calculated both by using the Marcus reorganization energy approach[6] and by calculating the electronic activation energy directly for a binuclear complex with one common water ligand in the second hydration shell. The rates for the inner-sphere reactions 2−4 were calculated for the binuclear complexes with bridging ligands in the first coordination sphere.

In the neptunyl complexes Np(VI) has one and Np(V) two unpaired f-electrons, resulting in more close-lying states than in the uranium case, which makes the identification of the ground state more difficult. In addition, the spin−orbit effects, which were negligible for uranium, become more important; the spin−orbit effects are analyzed in detail in a separate article.[7]

Because reactions 1−4 involve a fast electron-transfer step, long range solvent effects cannot be described in the usual way by a polarizable continuum model (PCM) in equilibrium with the complex. In the uranium study all calculations were done in the gas phase and the solvent effects were estimated from the Marcus formula.[6] For the outer-sphere reaction, this gives a reasonable estimate of the solvent effects whereas only an upper limit is obtained for the inner-sphere reactions. In the present study we have used a nonequilibrium PCM model that approximates a medium where the solvent molecules are not allowed to reorient during the electron-transfer process.

2. Theory. Models and Technical Details

2.1. Electron-Transfer Process. The theory for the electron-transfer process is described in detail in ref 1, and here we will only give an outline.

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The rate constant for the total reaction is[8,9]

$$k_{\mathrm{obs}} = K_{\mathrm{A}}\kappa_{\mathrm{el}}\nu_{\mathrm{n}}\mathrm{e}^{-\Delta G^{\ddagger}/RT} \qquad (6)$$

where K_A is the equilibrium constant for the formation of an outer-sphere ion pair between the reactants in reaction 1 and of the binuclear complex in reactions 2−4, κ_{el} is the electronic transmission coefficient, ν_n the nuclear frequency factor and $\Delta G^{\ddagger}$ the activation free energy. The effective electron-transfer frequency factor ν_{eff} is defined as

$$\nu_{\mathrm{eff}} = \kappa_{\mathrm{el}}\nu_{\mathrm{n}}\mathrm{e}^{-\Delta G^{\ddagger}/RT} \qquad (7)$$

The electron transmission coefficient κ_{el} is given by

$$\kappa_{\mathrm{el}} = \frac{2(1 - \mathrm{e}^{-\nu_{\mathrm{el}}/2\nu_{\mathrm{n}}})}{2 - \mathrm{e}^{-\nu_{\mathrm{el}}/2\nu_{\mathrm{n}}}} \qquad (8)$$

where the electronic and nuclear frequency factors, ν_{el} and ν_{n} are

$$\nu_{\mathrm{el}} = \frac{2\pi {H_{12}}^2}{\hbar}\left(\frac{1}{4\pi\lambda RT}\right)^{1/2} \qquad (9)$$

$$\nu_{\mathrm{n}} = \left[\frac{\sum_i {\nu_i}^2 E_i}{\sum_i E_i}\right]^{1/2} \qquad (10)$$

H_{12} is the electron-transfer coupling element, λ is the reorganization energy, and E_i and ν_{i} are the energy change and frequency of the vibrational modes i that bring the reactants to the transition state. The reorganization energy of the first coordination sphere is defined in the Marcus theory[6] as

$$\lambda = E^{\mathrm{V}}(\mathrm{VI}) + E^{\mathrm{VI}}(\mathrm{V}) - E^{\mathrm{VI}}(\mathrm{VI}) - E^{\mathrm{V}}(\mathrm{V}) \qquad (11)$$

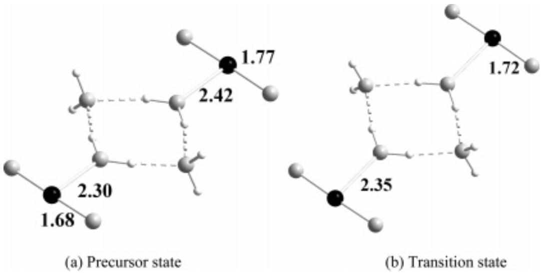
where $E^m(n)$ is the Gibbs free energy of the neptunyl complex in oxidation state m at the geometry of oxidation state n. The relationship between the reorganization energy and the activation energy is

$$\Delta G^{\ddagger} = \frac{\lambda}{4} \qquad (12)$$

Relation 12 is exact provided that the potential surfaces are quadratic.

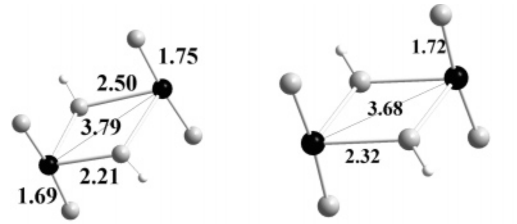
2.2. Outer- and Inner-Sphere Models. In the outer-sphere model it is assumed that the two neptunyl units have no common ligands. Both NpO_2^+ and NpO_2^{2+} are assumed to be coordinated by five water molecules in the equatorial plane.[10] We have used two models for this mechanism, the Marcus model where the activation free energy is calculated using eqs 11 and 12, and a direct model, where two neptunyl units are assumed to bind through an extended water bridge; in this model we have used the calculated electronic activation energy as an estimate of the corresponding activation free energy. In the direct model we have, as in ref 1, only included four water molecules, leaving the first hydration shell unsaturated. Figure 1 shows the structure of the precursor and transition state for this complex.

In the inner-sphere reaction mechanism the precursor complexes are assumed to be connected through a double bridge, sharing two ligands in reactions 2 and 3 and one carbonate in reaction 4; the carbonate is assumed to be chelate bonded to both Np(V) and Np(VI). As in the outer-sphere direct model the first hydration shells were left unsaturated, with only the bridging ligand in the first coordination sphere. The accuracy of this approximation is discussed in ref 1; in the outer-sphere uranyl electron-transfer reaction the Marcus model with only one water in the first hydration sphere gives an error of 6 kJ/mol on the activation energy, compared to the model with a fully saturated first hydration sphere. We expect a similar error for the inner-sphere reactions. The hydroxide, fluoride and carbonate complexes are shown in Figure 2a−c.

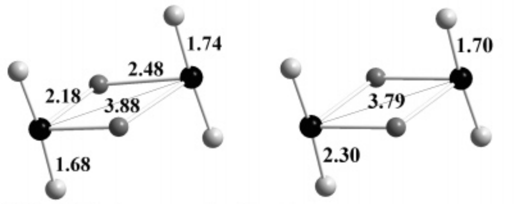


(a) Precursor state (b) Transition state

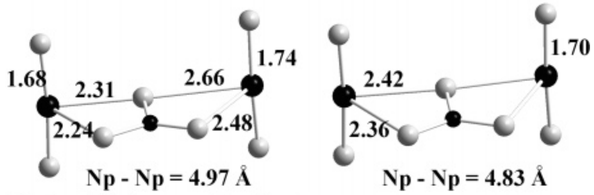
Figure 1. Geometry of the precursor (a) and transition state (b) of the $(NpO_2)_2(H_2O)_4^{3+}$ complex. The point symmetry is C_{2v} and D_{2h} for the precursor and transition state, respectively. In the transition state the two neptunyl units are equivalent. Bond distances in Å.



(a) Hydroxide bridged precursor and transition state



(b) Fluoride bridged precursor and transition state



(c) Carbonate bridged precursor and transition state

Figure 2. Geometry of the precursor and transition state of (a) $(NpO_2)_2(OH)_2^+$, (b) $(NpO_2)_2F_2^+$, and (c) $(NpO_2)_2CO_3^+$ complexes. In the transition state the neptunyl units are equivalent. Bond distances in Å.

At the transition state the neptunyl ions must be equivalent. This follows from the fact that a nuclear configuration must be either at a maximum (or a cusp if the state is degenerate, because of the Jahn−Teller instability) or a minimum on the potential surface.[11] As discussed in ref 1 the calculation method results in localization of the wave function at the transition state, with two f-electrons on one neptunyl and one on the other. A proper solution is therefore obtained by symmetrizing the wave functions Ψ^{L} and Ψ^{R} and solving the resulting 2 × 2 nonorthogonal CI problem. The transition state geometry was obtained by optimizing the geometry of the binuclear complex at the SCF level, imposing the proper symmetry on the molecular orbitals. The electron-transfer coupling element H_{12} required for estimating the electron-transfer rates (see eq 9), is equal to the half of the splitting between the states obtained from the 2 × 2 CI. The models for the reactions and the electron localization are discussed in more detail in ref 1.

2.3. Solvent Effects. The solvent polarization in the presence of charged complexes will contribute to the reaction energy and Marcus[6] has derived an estimate of this contribution to the reorganization energy for an outer-sphere electron-transfer process

$$\lambda^{\mathrm{sol}} = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R_{12}}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \tag{13}$$

where a_1 and a_2 are the radii of the cavities around the metal centers including their first hydration shells, R_{12} is the distance between them and ϵ_0 and ϵ_∞ are the static and dynamic dielectric constants of the solvent. In eq 13 it is implicitly assumed that the complexes are rather far apart, and the equation is thus applicable only for outer-sphere reactions.

The inner-sphere reactions are more difficult to describe. In the precursor state the wave function is localized with two f-electrons on one neptunyl and one on the other, and it remains so as the system is approaching the transition state. The wave function will become symmetrical in the immediate vicinity of the transition state if the two components Ψ^{L} and Ψ^{R} are allowed to interact. Technically, this is achieved through a 2 × 2 nonorthogonal CI. In an equilibrium PCM applied to one of the components, the solvent will be polarized in a field describing the charge distribution prior to the electron transfer. Formulated differently, the molecules in the solvent will not have time to reorient in the localized model because the transfer of an electron is fast compared to the nuclear movements.

It is important to make a distinction between the static part of the solvent polarization (the orientation of the solvent molecules) and the dynamic part (the electronic response), where the static part is slow but the dynamic fast. Thus, in an electron-transfer process the dynamic part will adjust to the electronic wave function during the reaction, whereas the static part will not.

The equilibrium PCM is thus not applicable when describing electron-transfer processes. Solvent effects for inner-sphere reactions can instead be described by using a nonequilibrium PCM model.[12] At the transition state the static polarization should describe the solvent with the delocalized charge distribution and this static polarization should be used to calculate the energy of the localized single component wave function.

As discussed in ref 1, the solvent effect should increase the activation energy. This can be seen directly from eq 13 where $\epsilon_0 \gg \epsilon_\infty$. Because the inner-sphere complexes have a more compact charge distribution and smaller multipole moments (because the inter-nuclear distances are smaller), it can be expected that the changes in solvent polarization in the electron-transfer process will also be small. Thus the solvent contributions to the activation energy for the electron-transfer process are expected to be smaller for the inner-sphere reactions than for the outer-sphere process. This is also illustrated by the distance dependence of the reorganization energy in eq 13.

Additional details of the nonequilibrium PCM calculations are given in sections 3.3.1 and 3.3.2.

2.4. Technical Details. Effective core potentials of the Stuttgart type[13] were used in all calculations. Previous studies[14−17] have demonstrated their accuracy in actinide systems. The first row atoms were described using the energy-adjusted ECPs suggested by Bergner et al.[18] augmented with a polarizing d-function. For neptunium, we used the small core ECP[13,19] with the 5s, 5p, 6s, 6p, 5d, 6d, 5f, and 7s electrons in the valence, all together 33 electrons, and for hydrogen we used the basis set suggested by Huzinaga[20] with 5s functions contracted to 3s and one polarizing p-function. The geometries were calculated using a small basis set without polarization functions, whereas a larger basis set with polarization functions on the first row atoms and on hydrogen atoms was used for the energy calculations. The basis set for Np was augmented with two g-functions in the single point calculations. The effect of the g functions was found to be small, which is similar to the results on the corresponding uranyl complexes.[16]

Geometries for the inner-sphere model complexes were optimized in the gas phase at the SCF level. For the water-bridged outer-sphere model, the geometry was optimized using the PCM model[21] at the SCF level, because in the gas phase the precursor state dissociated. Total energies were calculated at the CASPT2 level on the basis of a minimal CAS space, which is equivalent to MP2 for a closed shell system. This procedure was shown to give reliable results in ref 1. The nonorthogonal CI needed to calculate the energy of the symmetrized wave function with localized molecular orbitals was done using the RASSI module of the MOLCAS6[22] program system.

It is well-known that the error in the Np−$\mathrm{O_{yl}}$ bond distance at the SCF level is significant. The consequences of this deficiency are minor, in particular for the calculation of the reorganization energy, as discussed in ref 1.

The spin−orbit integrals were calculated in the mean-field approximation[23a,b] with the AMFI program[24] using the method described in refs 25 and 26. The spin-free wave functions were obtained at the CASSCF level using MOLCAS6. The spin−orbit effects presented here were calculated at the variation−perturbation level using the RASSI-SO module in MOLCAS6.[22] Technical details and an analysis of the spin−orbit effects on the neptunyl complexes is given by Fromager et al.[7]

3. Results

3.1. Outer-Sphere Reaction. Reaction 1, $\mathrm{NpO_2^{+}(aq)} + \mathrm{NpO_2^{2+}(aq)} \rightleftharpoons \mathrm{NpO_2^{2+}(aq)} + \mathrm{NpO_2^{+}(aq)}$, was studied using both the direct model and the Marcus model described in section 2.2. The precursor and the transition state for the direct model are shown in Figure 1, where also the interatomic distances are indicated. The calculated activation energies are shown in Table 1.

The activation energy was calculated both by direct means and by using eqs 12 and 13 for the binuclear complex. The difference between the two energies gives a measure of the quadratic character of the potential surface. This difference is quite small, below 3 kJ/mol at the spin-free level for both the uranium and neptunium complexes; the spin−orbit effects reduce this difference to only 0.1 kJ/mol for the neptunium complex. The potential surface is thus very close to quadratic. It should be mentioned that the Marcus model gives the Gibbs activation free energy, whereas the direct calculation gives the electronic activation energy. However, similar structures of the precursor and the transition state imply that the electronic effects dominate the magnitude of the barrier. The spin-free activation energy for neptunium is higher than for uranium by 9 kJ/mol at the SCF level, and about 5 kJ/mol at the minimal CASPT2 level. These differences are presumably due to the shorter bond distances in the Np complexes. The spin−orbit effect lowers the activation energy by 3 kJ/mol, reducing the difference to 1.6 kJ/mol.

TABLE 1: Activation Energy Calculated as the Energy Difference between the Transition State and the Precursor State or from the Reorganization Energy of the Neptunyl and Uranyl Dimers Bridged by the Four Waters in the Gas Phase[a] (SCF Values Included for Reference)

	SCF		minimal CASPT2		SO[c]	
model	λ^b	$\Delta G^\ddagger$ (=λ/4)^b	λ^b	$\Delta G^\ddagger$ (=λ/4)^b	λ^b	$\Delta G^\ddagger$ (=λ/4)^b
transition state U[d]		21.1		18.7	no effect	
reorg energy in water bridged U[d]	84.3	21.1	63.5	15.9		
transition state Np		29.9		23.1		20.3
reorg energy water bridge Np	126.7	31.7	82.3	20.6	80.9	20.2

[a] The geometries are optimized using the PCM. [b] In kJ/mol. [c] The spin−orbit effects (added to the minimal CASPT2 energies) are obtained by calculating the SO lowering of the ground state on both fragments $\mathrm{Np^{VI}(H_2O)_4{}^{2+}}$ and $\mathrm{Np^{V}(H_2O)_4{}^{+}}$. See details in ref 7. [d] From ref 1.

TABLE 2: Reorganization Energy in the Gas Phase Calculated at the SCF, Minimal CASPT2, and SO Levels from Single An(VI) and An(V) Complexes (An = U, Np) with Five Waters[a] (SCF Values Included for Reference)

	SCF		minimal CASPT2		SO[b]	
system	λ	$\Delta G^\ddagger$	λ	$\Delta G^\ddagger$	λ	$\Delta G^\ddagger$
U[c]	102.3	25.6	58.5	14.6	no effect	no effect
Np	128.8	32.2	85.1	21.3	80.2	20.1

[a] Both the SCF and minimal CASPT2 values are calculated with the larger basis set. The geometries are calculated at the SCF level in gas phase with a small basis set. All the energies are given in kJ/mol. $\Delta G^\ddagger = \lambda/4$, where λ is the reorganization energy. [b] The spin−orbit effects (added to the minimal CASPT2 energies) are obtained for the Np(VI) and Np(V) complexes coordinated with five waters molecules in the equatorial plane (see ref 7). [c] From ref 1.

The activation energy obtained with the outer-sphere Marcus model, obtained by applying eq 11 and 12 to the hydrated complexes $[\mathrm{NpO_2(H_2O)_5}]^{2+}$ and $[\mathrm{NpO_2(H_2O)_5}]^{+}$ is shown in Table 2. The activation energies are slightly larger than those obtained with the direct model, 2 kJ/mol at the spin-free level. The spin−orbit effect on the activation energy is slightly smaller than that obtained with the direct model, making the results at the spin−orbit level almost the same. The smaller spin−orbit effect found in the Marcus model is possibly due to a more efficient quenching because a complete first coordination coordination sphere was used. The activation energy in the gas phase is about 5 kJ/mol higher than that obtained for the uranium complexes. The error in the calculated barriers is difficult to estimate, but from the comparisons in section 3.6 they appear to be below 10 kJ/mol.

3.2. Inner-Sphere Reactions. The precursor and the transition state of the neptunyl complexes with hydroxide, fluoride and carbonate bridges are shown in Figure 2. The interatomic distances are indicated in the pictures, together with the distances for the corresponding uranyl complexes in parentheses. The differences between the uranyl and the neptunyl complexes are minor.

The calculated activation energies are shown in Table 3. At the spin-free level the gas-phase energies at the crossing points, calculated for one component at the SCF level, are about 5 kJ/mol higher than those obtained for the corresponding uranium reactions. At the minimal CASPT2 level the gas-phase energies at the crossing points are 5 kJ/mol higher for the fluoride and the carbonate bridges as compared to the uranium results, whereas it is 5 kJ/mol lower for the hydroxide bridge.

3.3. Solvent Effects. *3.3.1. Inner-Sphere Reactions.* The Marcus equation, eq 13, is applicable only for the outer-sphere complexes, and the only conclusion we can make for the inner-sphere reactions on the basis of this equation is that the solvent effect should be smaller than for the outer-sphere reaction due to the decrease of the reorganization energy with deceasing R_{12}. This is consistent with the fact that the charge is transferred over a shorter distance in the inner sphere, than in the outer-sphere complex, and thus the overall changes in the solvent polarization due to the electron transfer should be smaller for the inner-sphere case.

As discussed in the Theory, the electron transfer is a fast process compared to the reorientation of the water molecules, and only the dynamic part of the solvent polarization (electronic response) is in equilibrium with the electronic wave function during the electron transfer. The static part, which is the major contributor to the large static dielectric constant of water, is too slow to adjust to the changed field. Thus a standard equilibrium PCM model cannot be used, but nonequilibrium PCM models, where the static polarization is frozen from some pertinent nuclear and electronic arrangement, are applicable. There are two possible ways in which the nonequilibrium PCM can be applied in the present context. The first is to calculate the activation energy from the reorganization energy as in the Marcus theory. The only prerequisite for this is that the surfaces have to be quadratic. The reorganization energy is then obtained from an equation similar to eq 11, where $E^{\mathrm{V}}(\mathrm{VI}) + E^{\mathrm{VI}}(\mathrm{V})$ is replaced by the energy of the successor using the geometry and the static polarization from the precursor, and $E^{\mathrm{V}}(\mathrm{V}) + E^{\mathrm{VI}}(\mathrm{VI})$ by the energy of the precursor in a normal equilibrium PCM. The second possibility, which we have chosen to use, is to calculate the energy of the localized one component wave function at the transition state in the static PCM field generated by a symmetric transition state (with the same number of f-electrons on both neptunium centers). In both methods only the static part of the solvent polarization is kept frozen, whereas the dynamic part of the solvent response is allowed to relax to the actual charge distribution. We have chosen the latter method, because it is consistent with our method to find the transition state. Both methods will give the same results as long as the potential energy surfaces are quadratic; this was checked for the fluoride bridge.

Technically, the symmetric static solvent polarization was obtained from equilibrium PCM calculations at the transition state with frozen symmetric f-orbitals, which guaranteed 1.5 f-electrons on each neptunium center. The f-orbitals were obtained from a calculation in the gas phase using symmetrical SCF orbitals as the starting point, but allowing only a few iterations in RASSCF (until the wave function started to localize).

It is not evident if it is reasonable to use nonequilibrium PCM on our simple model complexes with unsaturated first hydration shells. In the nonequilibrium PCM model the strong polarization of the dielectric continuum replacing the water molecules in the first hydration shell could create artificial effects on the activation energies. To test if this is a problem, we did a calculation on the inner-sphere uranyl complexes with fluoride and hydroxide bridges augmented by six additional water molecules which filled the first hydration shells of both metal centers.

TABLE 3: Energy Differences between the Transition and Precursor States for the Neptunyl and Uranyl Complexes with Hydroxide, Fluoride, and Carbonate Bridges at the Minimal CASPT2 (Basis Set with d Functions Used on Oxygen, Fluoride, and Carbon Atoms) and the SO Level in the Gas Phase (SCF Values Included for Reference)

	precursor	transition state	bridge ligand	SCF one component[b]	minimal CASPT2 one component[b]	minimal CASPT2 symmetrized[a,b]	SO[b,c]
U[d]	C_2	C_{2h}	hydroxide	48.2	39.2	36.2	no effect
	C_{2h}	D_{2h}	fluoride	48.1	40.5	37.8	
	C_s	C_{2h}	carbonate	44.3	36.0	34.6	
Np	C_2	C_{2h}	hydroxide	53.1	34.6	33.3	28.1
	C_{2v}	D_{2h}	fluoride	53.2	45.8	42.8	38.8
	C_s	C_{2v}	carbonate	52.3	41.1	38.0	34.0

[a] The symmetrization correction is obtained at the SCF gas-phase level. [b] In kJ/mol. [c] The spin−orbit effects (added to the minimal CASPT2 symmetrized energies) are obtained using the fragment method (see ref 7). [d] From ref 1.

TABLE 4: Contribution of the Solvent Effects to the Activation Energy in the Inner-Sphere Model for the Uranyl and Neptunyl Complexes Calculated at the SCF and Minimal CASPT2 One-Component Level Using the Nonequilibrium PCM (SCF Values Included for Reference)

	SCF one component			minimal CASPT2 one component		
bridge ligand U	gas phase	PCM noneq	ΔPCM	gas phase	PCM noneq	ΔPCM
hydroxide	48.2	51.1	2.9	39.2	40.7	1.5
hydroxide + 6H_2O	45.2	52.5	7.2	34.4	39.3	4.9
fluoride	48.1	57.3	9.1	40.5	45.7	5.2
fluoride + 6H_2O	43.1	54.5	11.4	34.1	42.3	8.2
carbonate	44.3	51.1	6.8	36.0	40.2	4.2

	SCF one component			minimal CASPT2 one component		
bridge ligand Np	gas phase	PCM noneq	ΔPCM	gas phase	PCM noneq	ΔPCM
hydroxide	53.1	63.4	10.3	34.6	43.8	9.2
fluoride	53.2	67.3	14.1	45.8	52.7	6.9
carbonate	52.3	57.9	5.6	41.1	42.4	1.3

[a] ΔPCM is the difference between the PCM nonequilibrium and gas-phase energies. Energies in kJ/mol.

TABLE 5: Coupling Term H_{12} between the States $(\Psi^R)_i$ (i = 1, 2) and $(\Psi^L)_i$ (i = 1, 2) Calculated in the Gas Phase at the SCF Level for the Hydroxide Bridge

H_{12}[a]	$(\Psi^R)_1$ $E = -1121.06170994$ au	$(\Psi^R)_2$ $E = -1121.06186954$ au
$(\Psi^L)_1$ $E = -1121.06171010$ au	1.74	0
$(\Psi^L)_2$ $E = -1121.06186954$ au	0	0.7
(H_{12}^{eff})[a]	1.3	

[a] In kJ;mol.

TABLE 6: Coupling Term H_{12} between the States $(\Psi^R)_i$ (i = 1, 2) and $(\Psi^L)_i$ (i = 1, 2) Calculated in the Gas Phase at the SCF Level for the Carbonate Bridge

H_{12}[a]	$(\Psi^R)_1$ $E = -1141.18380364$ au	$(\Psi^R)_2$ $E = -1141.18366420$ au
$(\Psi^L)_1$ $E = -1141.18380364$ au	0.28	0.66
$(\Psi^L)_2$ $E = -1141.18366420$ au	0.66	3.18
(H_{12}^{eff})[a]	2.4	

[a] In kJ/mol.

The nonequilibrium PCM effects obtained with the model with an unsaturated first hydration shell and the model with six additional water molecules differ, at the PT2 level, by about 3.4 kJ/mol for the hydroxide complex; see Table 4. The total activation energies differ even less, about 1.4 kJ/mol on both SCF and MP2 levels. The corresponding numbers for the fluoride complex are 3.0 and 2.4 kJ/mol. From these results we conclude that at least for the inner-sphere reactions, the simple models with an unsaturated first hydration shell are suitable for the nonequilibrium PCM calculations.

There are systematic differences between the PCM effect at both the SCF and the PT2 levels; the nonequilibrium PCM effect is always a few kJ/mol smaller at the correlated level than at the SCF level. The reason is that we use the solvent polarization generated at the SCF as a static perturbation in the correlated calculation. Because dynamic correlation in general leads to a more compact charge distribution, the total interaction energy will be smaller than that of the SCF charge distribution. The total energy difference between the gas phase and PCM calculation is 20% higher in the SCF calculation than in the minimal CASPT2 calculation for the fluoride-bridged complex. With such a large difference it is not surprising that the PCM effect is somewhat smaller at the correlated level than at the SCF level. We have for consistency reasons chosen to use the correlated rather than the SCF results as the bases for further analysis, although this choice is somewhat arbitrary.

The total activation energies calculated at the nonequilibrium PCM level for the uranyl complexes with hydroxide, fluoride, and carbonate bridges are 40.7, 45.7, and 40.2 kJ/mol, respectively, as compared to 43.8, 52.7, and 42.4 kJ/mol for the corresponding neptunyl complexes at the spin-free level. That means that the activation energies at the spin-free level are somewhat higher (2−7 kJ/mol) for the neptunyl than for uranyl inner-sphere complexes, but this is of the same order as our error estimate (the error appears to be below 10 kJ/mol; see section 3.2).

3.3.2. Outer-Sphere Reactions. As discussed in section 2.4 the standard method to estimate the solvent polarization contribution to the reorganization energy and thus the activation energy is given by the Marcus equation (eq 13). Applying this equation to the outer-sphere complex with the water dielectric constants $\epsilon_0 = 80$, $\epsilon_\infty = 1.78$, the radii $a_1 = 4.315$ Å and $a_2 = 4.390$ Å, and $R_{12} = 8.19$ Å results in a solvent contribution of 20 kJ/mol. The radii are based on the optimized geometries of $NpO_2(H_2O)_5^{2-}$ and $NpO_2(H_2O)_5^{-}$, the van der Waals radii of the atoms, and the optimized Np−Np distance in the bridge model. The corresponding solvent polarization contribution in the uranium complexes studied in ref 1 was 18 kJ/mol.

The accuracy of the nonequilibrium PCM was investigated for the uranyl complexes in both the Marcus and the bridged models. The nonequilibrium PCM effect was in both cases more than a factor of 2 larger than that obtained by the Marcus equation with a U−U distance from the bridge model transition state ($R_{12} = 8.19$ Å). Our interpretation is that the solvent effect is overestimated by the nonequilibrium PCM, probably because

TABLE 7: Relative Electron-Transfer Rates in the Solvent Phase for the Electron Transfer with the Uranyl and Neptunyl Complexes for Different Reaction Paths after the Precursor Complex Is Formed[a]

model	An(VI)−An(V) distance (Å)	H_{12}[b] (kJ/mol)	$\Delta G^{\ddagger}$ (kJ/mol)	ν_{el} (s^{-1})	κ_{el}	ν_{eff} (s^{-1})
U[c]						
hydroxide	3.74	3.03	37.7	1.332×10^{13}	0.35	2.849×10^{6}
fluoride	3.77	2.67	43.0	9.635×10^{12}	0.28	2.23×10^{5}
carbonate	4.86	1.37	38.8	2.671×10^{12}	0.09	3.97×10^{5}
outer sphere	8.25	0.011	36.7	1.770×10^{8}	6.39×10^{-6}	6.59×10^{1}
Np						
hydroxide	3.68	1.3	37.3	2.453×10^{12}	0.08	6.74×10^{5}
fluoride	3.79	3.1	45.6	1.261×10^{13}	0.32	9.76×10^{4}
carbonate	4.83	2.4	35.3	8.592×10^{12}	0.24	4.60×10^{6}
outer sphere	8.19	0.05	40.6	3.477×10^{9}	1.19×10^{-4}	2.68×10^{2}

[a] The nuclear frequency factor ν_n is assumed to be 2.93×10^{13} s^{-1} for neptunyl and 2.77×10^{13} s^{-1} for uranyl (based on the average $\mathrm{NpO_{yl}}$ and $\mathrm{UO_{yl}}$ bond stretching frequencies). Solvent effects are calculated with the nonequilibrium PCM in the inner-sphere model and the dielectric continuum model derived by Marcus in the outer-sphere model. [b] Calculated in gas phase. [c] In ref 1 the denominator in ν_{el} had not been modified to include the solvent effect. This has been corrected in the present work. The effect is minor (cf. ref 1).

of the different charges on the V and VI complexes. It is reasonable to assume that the large polarity of the bridge complexes should give rise to similar problems. The Marcus equation on the other hand is constructed to describe a charge-transfer process.

For the inner-sphere reactions the charge effect is less pronounced because the inter-nuclear distances are shorter and the polarity problem thus smaller. The fact that the solvent effect on the activation energy, calculated with the nonequilibrium PCM, is smaller for the inner-sphere reactions than the Marcus equation estimate for the outer-sphere reaction (as it should be because the complex is less polar) renders credibility to the calculated solvent effect on the inner-sphere reactions.

3.4. Electronic Coupling Elements. Assuming Np(V) to be located on the left-hand side in the $\mathrm{Np^{V}O_2{-}X{-}Np^{VI}O_2}$ complex, where X is the bridge, the squared electron coupling element $(\mathrm{H}_{12})^2$ appearing in the electronic frequency factor, eq 9, describes the probability of an electron transfer from Np(V) to the left to Np(VI) to the right. This probability depends on the thermal population of the ground and excited states of Np(V). If the excited states lies significantly, more than kT (about 2.5 kJ/mol), above the ground state, only the latter will be populated and H_{12} is equal to half the splitting obtained from the 2×2 nonorthogonal CI problem described in section 2.2 and ref 1. However, if there are excited states with excitation energies below 2.5 kJ/mol, the thermal occupation of the excited states must be considered when the probability for electron transfer is calculated. This implies that we have to introduce some averaging over the different states or, more conveniently, define an effective coupling element H_{12}^{eff}. This situation did not occur for the uranium systems, only for the neptunium hydroxide and carbonate complexes, where the first excited state is nearly degenerate with the ground state (with a splitting of 0.4 kJ/mol, well below kT). The ground state and the first excited state are thus almost equally populated at room temperature.

The effective coupling element H_{12}^{eff} is defined in such way that it includes all the summation and averaging over different initial and final states. Hence, the total rate of electron transfer can be obtained directly by eqs 6 and 9. The averaging must be done over probabilities; that is, ${H_{12}}^2$ in eqs 6−9 is equal to ${H_{12}}^2 = (H_{12}^{\mathrm{eff}})^2 = \sum_{i=1}^{N_{\mathrm{I}}} p_i \sum_{f=1}^{N_{\mathrm{F}}} (H_{12}^{\mathrm{if}})^2$, where p_i is the thermal population of the state i on the reactant side, N_{I} is the number of such degenerate initial states, and N_{F} is the number of degenerate final states. Note that because the states are nearly degenerate, there is no need to consider vibrational effects, the Franck−Condon factor is close to 1. The initial states are in thermal equilibrium, and because the states are almost degenerate, the probability to be in state i being $p_i = 1/N_{\mathrm{I}}$ (in our case $N_{\mathrm{I}} = 2$), recall that the final state with Np(V) to the right will not be in thermal equilibrium immediately after the electron transfer. The total rate therefore includes the summation over all the final states, but no thermal averaging over them (in our case $N_F = N_{\mathrm{I}} = 2$). The individual coupling elements H_{12}^{if} for the hydroxide and carbonate complexes are shown in Tables 5 and 6.

The electron coupling element H_{12} (H_{12}^{eff} for hydroxide and carbonate complexes), the electronic and effective frequency factors ν_{el} and ν_{eff}, and the electronic transmission coefficients κ_{el} are shown in Table 7.

The electron transfer is considered to be adiabatic if the electron coupling energy is larger than about 3 kJ/mol. The coupling energies for the inner-sphere reactions are, similar to the uranium case, not very far from this value, and from this consideration alone the processes would be judged as mainly adiabatic. The electron transmission coefficient κ_{el}, which approaches 1.0 in the adiabatic case, that is, for large H_{12} (see eqs 8 and 9), is between 0.1 and 0.3 for the inner-sphere reactions. The outer-sphere reaction is predominantly diabatic, with an electron transmission coefficient of only 1.19×10^{-4}. The neptunium and the uranium complexes are similar in this respect, the electron transmission coefficients differ at most by a factor of 3 between the inner-sphere reactions, which is not much in this context, whereas the difference between the outer-sphere reactions is larger. The relative rates in the solvent reactions, illustrated by the effective frequency factor ν_{eff} in Table 7 (see eq 7), are similar for all the reactions, the inner-sphere reaction in the carbonate complex being somewhat faster than the others. The effective frequency factors are similar for the neptunium and the uranium complexes.

3.5. Reaction Rates. Solvent effects decrease all reaction rates substantially due to the increase in $\Delta G^{\ddagger}$; the effect is large for the outer-sphere reactions. The reaction rate for the outer-sphere reaction can be calculated using the equilibrium constant for the formation of the precursor, obtained from the Fuoss equation; the latter is $\log K_{\mathrm{os}} = -0.60$ at zero ionic strength (and a Np−Np distance of 8.19 Å). The resulting calculated rate constant for the self-exchange reaction 1 at 25 °C is

$$k = 10^{-0.60} \times 2.68 \times 10^{2} = 67.3\ \mathrm{M^{-1}\ s^{-1}} \tag{14}$$

This value in fair agreement with the range of estimates, 0.0063−15 $\mathrm{M^{-1}\ s^{-1}}$, given by Howes et al.[4] on the basis of the Marcus cross-correlation method, and also in reasonable agreement with the direct experimental value given by Cohen et al.,[5] $k = 560\ \mathrm{M^{-1}\ s^{-1}}$, for the Np(V)−Np(VI) self-exchange reaction at 25 °C and an ionic strength of 0.1 M. The experimental activation energy for the latter reaction is 35 kJ/mol, again in fair agreement with the present result, 41 kJ/mol, but with a large uncertainty, as it is only based on data at two temperatures, 273 and 283 K; we estimate the error to at least 10 kJ/mol.

4. Conclusions

In the present study we have investigated the electron self-exchange between Np(V) and Np(VI) via inner- and outer-sphere mechanisms. The outer-sphere reaction was studied using both the Marcus model and a system with two actinide units connected by a water molecule in the second hydration sphere, whereas the inner-sphere reactions were studied directly on the bridged systems. Three topics have been investigated: the spin−orbit effect on the reaction, the solvent effects and differences between the self-exchange in the U(V)−U(VI) and the Np(V)−Np(VI) couples.

Because the electron-transfer process is fast compared to the nuclear movements, solvent effects must be described by a model where the solvent is not in equilibrium with the electronic part of the wave function during the electron transfer. We used the nonequilibrium PCM model and the Marcus equation for this purpose. It appears that the nonequilibrium PCM model overestimates the solvent effect for the outer-sphere reaction, presumably due to the change in charge, which is always difficult to describe with such models; in this case the standard Marcus equation was used instead. For the inner-sphere reactions the nonequilibrium PCM model appeared to perform better.

The barriers are usually somewhat higher for the neptunium system than for the uranium system, but the differences are not significant. Similarly, the differences in the reaction rates are small. The outer-sphere reactions are dominantly diabatic. The adiabatic contribution is of course much more important for the inner-sphere reactions, but their diabatic character is still significant (more than 50%). The calculated reaction rate for the outer-sphere reaction, 67.3 M^{-1} s^{-1}, is in reasonable agreement with the observed rates, 0.0063 to 15 M^{-1} s^{-1} based on the Marcus cross-correlation method. The calculated barrier, 41 kJ/mol, is in good agreement with an experimental estimate, 35 kJ/mol.

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Supporting Information Available: Coordinates, energies and structural parameters of optimized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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