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Spin−Orbit Effects in Electron Transfer in Neptunyl(VI)−Neptunyl(V) Complexes in Solution

Emmanuel Fromager,[†] Valerie Vallet,[*,‡] Bernd Schimmelpfennig,[§] Peter Macak,[||]
Timofei Privalov,[⊥] and Ulf Wahlgren[†]

Institute of Physics, Stockholm University, The AlbaNova University Center, S-10691 Stockholm, Sweden, Laboratoire PhLAM, UMR CNRS 8523, CERLA, Universitè des Sciences at Technologies de Lille, F-59655 France, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, D-76344 Eggestein-Leopoldshafen, Germany, Theoretical Chemistry, The Royal Institute of Technology, AlbaNova University Center, S-10691 Stockholm, Sweden, Organic Chemistry, Department of Chemistry, The Royal Institute of Technology, S-10044 Stockholm, Sweden

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The spin−orbit effects were investigated on the complexes involved in the electron self-exchange between Np(V) and Np(VI) in both the outer-sphere and inner-sphere mechanisms, the latter for binuclear complexes containing hydroxide, fluoride, and carbonate as bridging ligands. Results obtained with the variation−perturbation and the multireference single excitation spin−orbit CI calculations are compared. Both effects due to different relaxations of spinors within a multiplet (spin-orbit relaxation) and scalar (electrostatic) relaxation effects in the excited states are accounted for in the latter scheme. The results show that the scalar (electrostatic) relaxation is well described by the single-excitation spin−orbit CI, and that spin-orbit relaxation effects are small in the Np complexes, as in the lighter d-transition elements but in contrast to the main group elements.

1. Introduction

In previous articles we have investigated the electron self-exchange between U(V) and U(VI)[1] and Np(V) and Np(VI).[2] Neptunyl complexes have a more complicated electronic structure than the uranyl complexes; Np(VI) has one and Np(V) two unpaired f-electrons. This increases the significance of the spin−orbit effects on the computed barriers, which were negligible for uranium.[1] In the present paper we have made a detailed analysis of the spin−orbit effects on the electron self-exchange between neptunium species.

In ref 2, energy barriers and reaction rates were studied for the four different electron self-exchange reactions

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

$$\mathrm{NpO_2^{\ V}(OH)_2NpO_2^{\ VI} \rightleftharpoons NpO_2^{\ VI}(OH)_2NpO_2^{\ V}} \tag{2}$$

$$\mathrm{NpO_2^{\ V}F_2NpO_2^{\ VI} \rightleftharpoons NpO_2^{\ VI}F_2NpO_2^{\ V}} \tag{3}$$

$$\mathrm{NpO_2^{\ V}(CO_3)NpO_2^{\ VI} \rightleftharpoons NpO_2^{\ VI}(CO_3)NpO_2^{\ V}} \tag{4}$$

In all cases the reactants and the products are the same, and thus $\Delta G^\circ = 0$. The first reaction is of the outer-sphere type whereas reactions 2−4 are inner-sphere reactions. In the outer-sphere model it is assumed that two neptunyl units have no common ligands but are connected through the second coordination shell. In the inner-sphere reaction mechanism the precursor complexes are 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). The models used are described in ref 2 together with optimized precursor- and transition-state structures. The f-electrons remain localized during the reaction for the inner-sphere complexes, and the electron transfer takes place in the vicinity of the cusp where the potential surfaces describing the motion from the precursor to the transition state and the motion from the transition state to the successor state cross. The proper description of the transition state is thus a linear combination of the two (nonorthogonal) wave functions of precursor and successor type. For details of the models used and the computational procedures, see ref 2.

Here, we are concerned with the spin−orbit effects on the reaction barrier. The most common procedure for spin−orbit calculations on complexes of this type is to use the variation−perturbation (VP) method, where the spin−orbit interaction matrix is constructed in a limited wave function basis. The procedure is based on the LS coupling scheme and is paramount to assuming that spin−orbit effects and scalar correlation effects are not coupled. However, this is not evident, and when spin−orbit effects become significant, the question of the importance of jj-coupling, and in particular spin−orbit relaxation (different spatial extensions of the spinors in a multiplet), arises. In the present study we investigate the validity of the assumption that spin−orbit relaxation effects are small by using two different methods to calculate the spin−orbit effect; a variation−perturbation method and a multireference single excitation spin−orbit CI. The spin−orbit CI is based on a LS coupled basis set, and both the spin−orbit and the scalar relaxation effects are, as

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[*] Corresponding author. E-mail: valerie.vallet@univ-lille1.fr.

[†] Institute of Physics, Stockholm University, The AlbaNova University Center.

[‡] Laboratoire PhLAM, UMR CNRS 8523, CERLA, Universitè des Sciences et Technologies de Lille.

[§] Forschungszentrum Karlsruhe.

[||] Theoretical Chemistry, The Royal Institute of Technology, AlbaNova University Center.

[⊥] Organic Chemistry, Department of Chemistry, The Royal Institute of Technology.

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shown in this paper, properly accounted for by the interaction with the singly excited states.

2. Theory

2.1. Spin−Orbit Calculations. The spin−orbit effects were calculated both at the variation−perturbation level using the RASSI-SO module in MOLCAS 6[3] program package and by a two-step spin−orbit CI procedure using the EPCISO[4] program.

In the variation−perturbation calculations, a spin−orbit matrix is constructed in a basis consisting of all spin-free states in the f-manifold, that is, all states generated by distributing the f-electrons in the f-shells. The wave function basis is obtained by a simultaneous optimization of all states in a given symmetry with equal weights. In some cases, when the number of states becomes excessively large, states above a certain energy threshold are discarded from the basis. The result is then added to the spin-free energies obtained at some correlated level. It is thus tacitly assumed that the spin−orbit and the scalar correlation effects are additive.

In some cases, in particular among the main group elements, the coupling between spin−orbit and (scalar) correlation becomes significant, and this usually implies that a jj-coupled reference state would be preferable to a LS coupled one. The most obvious solution would then be to use a two- or four-component approach, but these methods become rather cumbersome for large CI expansions. However, if the dominant contribution to the jj-coupling effect is spin−orbit relaxation (differential spinor relaxation within a multiplet), an intermediate solution, based on a LS coupled basis set, becomes possible.

In the spin-free case orbital relaxation is defined as the difference between the orbitals used to construct the initial (trial) wave function (in our case the ground-state orbitals) and the self-consistent orbitals obtained at the Hartree−Fock level for some state (in our case the singly excited states). A single excitation CI is not strictly comparable to an SCF calculation, because the CI space is larger than the space spanned by the singly excited Brillouin states used to construct the Fock matrix; however, it is well-known that a single excitation CI (SCI) describes orbital relaxation effects well. Therefore, a spin-free multireference single excitation CI is able to recover most of the orbital relaxation effect in the states which constitute the reference space. A similar argument, as discussed in refs 4 and 5 can be used at the spin−orbit level. A multireference single excitation spin−orbit CI will thus at the same time describe spin-free (electrostatic) spinor relaxation and spin−orbit relaxation in all the states in the reference space. Consider, as an example, the thallium atom; the calculated splitting between the $^2P_{1/2}$ and the $^2P_{3/2}$ states is in general too small when calculated with the variation−perturbation method in a basis obtained by distributing three electrons among the 5s and 5p shells. Values reported in refs 6 and 7 are more than 1000 cm^{-1} too small at the variation−perturbation level in a basis obtained from the configurations s^2p^1, s^1p^2, and p^3 and Roos et al.[8] report a value of 7201 cm^{-1} in a large basis (the experimental splitting is 7793 cm^{-1}). A comparable spin−orbit CI gives an error of about 100 cm^{-1} (the remaining error is mainly due to core-valence correlation).[4]

In the two-step EPCISO program the first step is a spin-free SCF (or RASSCF) calculation to obtain an orbital basis. A set of determinants is generated in this orbital basis and used as the reference. In the second step, the Hamiltonian matrix for the multireference single excitation spin−orbit CI in the determinant basis is constructed and diagonalized. The spin−orbit splitting between the $^2P_{1/2}$ and the $^2P_{3/2}$ states of the thallium atom obtained using EPCISO[4] is 7762 cm^{-1}, compared to the experimental value 7793 cm^{-1}.

In the present calculations, all configurations in the f-manifold should ideally be used as the spin-free basis in both the variation−perturbation and the spin−orbit CI calculations. However, with three f-electrons and 14 f-orbitals, as in the inner-sphere reactions 2−4, the expansion becomes quite long, and in particular the orbital optimization step preceding the variation−perturbation calculation becomes cumbersome. Additional simplifications are thus desirable. One often uses the possibility to include only states with energy below a certain threshold. The effects of this approximation are investigated in section 3.1. An alternative is to exploit the fact that the spin−orbit operator falls as r^{-3}, which implies that the spin−orbit interaction is largely localized to the f-shells of the respective neptunyl units. If the complex is divided into fragments, each containing a single neptunyl unit and the bridge, spin−orbit calculations can easily be done separately for each fragment. The total spin−orbit effect is then obtained by adding the spin−orbit effects for the individual fragments. The fragments must of course have the same coordination and geometry as in the full complex. The accuracy of this procedure is investigated in section 3.2.

2.2. Technical Details. Relativistic effective core potentials of the Stuttgart type[9] were used in all calculations. Previous studies[10−13] have demonstrated their accuracy in actinide systems. The first row atoms were described using the energy-adjusted ECPs suggested by Bergner et al.[14] augmented with a polarizing d-function. For neptunium, we used the small core ECP[9] and the corresponding basis set[15] 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[16] 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. In the CASPT2 calculations the Np basis set was augmented with two g-functions.

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[17] at the SCF level, because in the gas phase the precursor state dissociates. 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 (see ref 1).

The spin−orbit integrals were calculated in the mean-field approximation[18,19] with the AMFI program[20] using the method described in refs 21 and 22. The spin−orbit calculations were done on the basis of ECP wave functions using the mapping procedure described in ref 21.

The spin-free wave functions were obtained at the CASSCF level using MOLCAS6. The variation−perturbation calculations were done using the RASSI module in MOLCAS6, and the spin−orbit CI calculations using the EPCISO program.

3. Results

3.1. Energy Thresholds. As discussed in section (2.1) only configurations below a certain threshold were included in the variation−perturbation calculations. The spin−orbit effect on the activation energy using different energy thresholds is shown in Table 1 for the fluoride bridge complex $(NpO_2)_2F_2^+$. The wave function basis was generated from multistate CASSCF

TABLE 1: Spin−Orbit Lowering of the Activation Energy Calculated for the Full Complex $(NpO_2)_2F_2^+$ Using RASSI-SO with Different Energy Thresholds

energy threshold (eV)	SO lowering for the precursor state (kJ/mol)	SO lowering for the transition state (kJ/mol)	SO lowering of the activation energy (kJ/mol)
1	103.19	110.16	6.97
2	111.84	118.55	6.71
2.5	114.98	121.53	6.55
4	115.69	122.11	6.42

TABLE 2: Energy Differences between the Transition and Precursor States in kJ/mol for the Neptunyl Complexes with Hydroxide, Fluoride, and Carbonate Bridges at the Minimal CASPT2 Level Using Symmetrized Wave Functions (See Ref 2) in the Gas Phase Including SO Effects

bridge ligand	RASSI-SO full complex	RASSI-SO fragments	EPCISO[a] fragments
hydroxide	26.5	28.1	23.5
fluoride	36.4	38.8	
carbonate		34.0	

[a] Including single excitations in the SO-CI.

TABLE 3: Comparison between the RASSI-SO and EPCISO Results on the $Np^{VI}(OH)_2$ and $Np^V(OH)_2^-$ Complexes in the Precursor State Geometry

code	fragment	states for which the orbitals are optimized	SO lowering of the GS (kJ/mol)
RASSI-SO	$Np^V(OH)_2^-$	GS + excited states	79.5
EPCISO (no singles)	$Np^V(OH)_2^-$	GS	71.5
EPCISO (with singles)	$Np^V(OH)_2^-$	GS	82.3
EPCISO (no singles)	$Np^V(OH)_2^-$	GS + excited states	79.9
EPCISO (with singles)	$Np^V(OH)_2^-$	GS + excited states	81.0
RASSI-SO	$Np^{VI}(OH)_2$	GS + excited states	33.3
EPCISO (no singles)	$Np^{VI}(OH)_2$	GS	18.0
EPCISO (with singles)	$Np^{VI}(OH)_2$	GS	32.0
EPCISO (no singles)	$Np^{VI}(OH)_2$	GS + excited states	33.3
EPCISO (with singles)	$Np^{VI}(OH)_2$	GS + excited states	35.0

calculations on the states in the f-manifold with equal weight on all configurations.

The spin−orbit effect on the activation energy by states higher than 2.5 eV above the ground state is negligible. On the basis of this result, thresholds of 4 and 3 eV were used in the calculations on the fluoride- and the hydroxide-bridged complexes, respectively. However, for the carbonate complex, further simplifications were necessary.

3.2. Fragment Method. In the fragment model (see section 2.1) spin−orbit calculations were done on two fragments containing a single neptunyl unit and the bridge, each fragment having the same coordination and geometry as the full complex. This means, for example, that for the fluoride bridge (reaction 3) the two fragments are $[Np^{VI}O_2F_2]$ and $[Np^VO_2F_2]^-$, with geometrical parameters from the full complex. The total spin−orbit effect is obtained by adding the spin−orbit effects for the individual fragments. The fragment method can be used straightforwardly for the precursor state; at the transition state it was applied on one component of the localized wave function (see ref 2).

The accuracy of this procedure was tested on the inner-sphere complexes with hydroxide and fluoride bridges at the variation−perturbation level. The calculations on the fragments were done in the complete f-manifold without energy thresholds. The basis for the spin−orbit calculations was generated from multistate RASSCF calculations with equal weight on all configurations. The results for hydroxide and fluoride-bridged complexes are shown in Table 2. The fragment method is quite accurate; the total spin−orbit effect is underestimated by about 2 kJ/mol, as compared to the calculation on the full complex. For the carbonate complex at the variation−perturbation level, and in all spin−orbit CI calculations, only the fragment method was used.

3.3. Spin−Orbit CI vs the Variation−Perturbation Method. The reference space used in the variation−perturbation and the spin−orbit CI included all configurations in the f-manifold for the fragment calculations and for the hydrated complexes used in the Marcus model (outer-sphere electron-transfer pathway), whereas an energy threshold was used for the hydroxide and fluoride complexes. The spin−orbit CI calculations were done both with all single excitations from the f-shell in all the reference states and, for the analysis, by diagonalizing the Hamiltonian in the reference space without the single excitations (prediagonalization). Two sets of molecular orbitals were used in these calculations: ground-state orbitals and state-averaged orbitals. In the variation−perturbation calculations only RASSCF averaged orbitals were used.

The importance of spin−orbit relaxation and the extent to which the scalar (electrostatic) orbital relaxation in the reference states is described by the single excitation spin−orbit CI was investigated for the fragments $Np^V(OH)_2^-$ and $Np^{VI}(OH)_2$ in the precursor-state geometry. The results are shown in Table 3. The single excitation CI, with ground-state orbitals, gives an energy lowering by spin−orbit effect of 32 kJ/mol for the Np(VI) complex, very close to the corresponding variation−perturbation result, 33.3 kJ/mol. The prediagonalization result, based on the ground-state orbitals, is 18 kJ/mol, 14 kJ/mol less than the single excitation CI result. The prediagonalization based on averaged orbitals gives the expected 33.3 kJ/mol, whereas the corresponding single excitation CI gives 35 kJ/mol.

In the Np(V) complex the ground state from the single excitation CI, using ground-state orbitals, is 82.3 kJ/mol below the spin-free ground state. The corresponding variation−perturbation result is 79.5 kJ/mol, and the single excitation spin−orbit CI with state-averaged orbitals gives 81.0 kJ/mol. The prediagonalization using ground-state orbitals gives 71.5 kJ/mol, 11 kJ/mol less than the single excitation CI result. Prediagonalization using state-averaged orbitals gives 79.9 kJ/mol; the difference between this result and the result from the variation−perturbation calculations, 79.5 kJ/mol, is due to a slightly different orbital optimization procedure. In the variation−perturbation scheme the orbitals were optimized separately for the high- and low-spin states, whereas only orbitals averaged for the high-spin states were used in the spin−orbit CI.

Two conclusions can be drawn from these results. First, the close agreement between the single excitation spin−orbit CI using ground-state and state-averaged orbitals shows that the spin−orbit CI is capable of reproducing, to a high degree of accuracy, the scalar (electrostatic) relaxation effects in the excited reference states. Second, the close agreement between the single excitation spin−orbit CI and the variation−perturbation results (obtained with state-averaged orbitals) shows that spin−orbit relaxation effects are small. It is generally assumed that jj-coupling effects are small for transition elements with open shells with high *l*-values;[23] our results confirm this assumption for the early actinides.

For the p-shells in the main group elements spin−orbit relaxation effects may be significant, for example, in thallium,[4,6,7] tellurium[24] and the heavy halogens.[5] It appears that the spin−orbit relaxation constitutes the major contribution to the jj-coupling in the main group elements, which is not surprising, because in perturbation theory the spin−orbit relaxation diagrams appear at the second-order in the energy whereas the fine structure correlation diagrams are at least of the third-order.[5]

Let us finally underline that the spin−orbit CI method has some practical advantages compared to the variation−perturbation method because there is no need to use state-averaged orbitals, which are often difficult to obtain.

4. Conclusions

In the present study we have investigated the spin−orbit effect on the activation energy in electron self-exchange reaction between Np(V) and Np(VI) via inner- and outer-sphere mechanisms.

Spin−orbit effects are more important in the Np system than in the U system.[2] It is generally assumed that scalar correlation and spin−orbit effects are largely decoupled in the transition elements and in the actinides. This assumption was investigated in detail by comparing results obtained from variation−perturbation calculations in the f-manifold with single excitation multireference spin−orbit CI results. The results show conclusively that this assumption is valid for high-valent actinides with open f-shells. In addition, it was found that the single excitation CI to a large extent is capable of describing the “spin-free” (electrostatic) relaxation of the orbitals used in the reference. Accurate results are obtained using only orbitals optimized for the ground state.

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