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Ab Initio Studies of Np and Pu Complexes and Reactions in the Gas Phase: Structures and Thermodynamics

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Reaction enthalpies for the reactions $2MO_3(g) + MF_6(g) \rightarrow 3MO_2F_2(g)$, $MO_2F_2(g) + 2H_2O(g) \rightarrow MO_2(OH)_2(g) + 2HF(g)$, $MF_6(g) + 2H_2O(g) \rightarrow MO_2F_2(g) + 4HF(g)$, $MO_3(g) + H_2O(g) \rightarrow MO_2(OH)_2(g)$, and $MF_6(g) + 3H_2O(g) \rightarrow MO_3(g) + 6HF(g)$ have been calculated at the CCSD(T) level for M = U and Np and at the MP2 level for M = U, Np, and Pu. The results are compared with previous calculated reaction enthalpies for M = U. The errors in the calculated reaction enthalpies are estimated to be below 20 kJ/mol for Np and about 50 kJ/mol for Pu.

1. Introduction

Gas-phase reactions involving actinides are important in connection with nuclear power production. For example, at the high temperatures in a core melt down, the nuclear fuel may react with water to give species such as $UO_2(OH)_2(g)$ in significant amounts. However, there is very little experimental and theory-based information on reactions of this type for the actinide elements. In a previous study we have calculated the Gibbs energy and enthalpy of reaction, $\Delta_r G°_m$ and $\Delta_r H°_m$, for a number of reactions between gas-phase species containing U(VI), F, O, and H.[1] Compilations and critical evaluations of thermodynamic data, $S_m°$, $C°_{p,m}$, $\Delta_f G°_m$, and $\Delta_f H°_m$, are given in refs 2 and 3; these data were used in ref 1 to calculate the "experimental" Gibbs energy and enthalpy of reaction, but the accuracy of these data is rather low. The theoretical calculations in ref 1 were done in the framework of quantum chemistry, with rather small basis sets. In this type of calculation one relies on the cancellation of errors that may be significant, depending on the systems under study. The initial results in ref 1 were rather poor, but a closer scrutiny showed a systematic error (associated with a mismatch in the description of the H−F and M−F bonds) that could be eliminated through a calibration procedure described below. The calibrated result showed a remarkable agreement with the "experimental" data, well within the experimental error bars; indeed the accuracy of the theoretical results may well be better than the accuracy in the calculated "experimental" numbers. This result makes it possible to calculate thermodynamic quantities, with high or reasonable accuracy, for other actinides where no experimental information is available.

In ref 1 the enthalpy and entropy of reaction were calculated at 298.15 K for the following reactions with M = U:

$$2MO_3(g) + MF_6(g) \rightarrow 3MO_2F_2(g) \tag{1}$$

$$MO_2F_2(g) + 2H_2O(g) \rightarrow MO_2(OH)_2(g) + 2HF(g) \tag{2}$$

$$MF_6(g) + 2H_2O(g) \rightarrow MO_2F_2(g) + 4HF(g) \tag{3}$$

$$MO_3(g) + H_2O(g) \rightarrow MO_2(OH)_2(g) \tag{4}$$

$$MF_6(g) + 3H_2O(g) \rightarrow MO_3(g) + 6HF(g) \tag{5}$$

In the present study we have extended this investigation to M = Np and Pu, for which no experimental data are available. As in ref 1, the entropy and heat capacity of reactants and products were calculated by using the vibration and rotation partition functions based on geometries and vibrational frequencies obtained by the quantum chemical methods. In ref 1 we found that while the best theoretical results, obtained with the CCSD(T) procedure, were in excellent agreement with experiment for reactions 1 and 4, this was not the case for reactions 2, 3, and 5, where the mismatch in the description of the H−F and the M−F bonds gave rise to the systematic error mentioned above in the calculated energies for these reactions. Calibrating the results to a reaction involving M and HF eliminated the systematic error; in ref 1 reaction 3 above was selected for the purpose. The procedure amounts to shifting the reaction enthalpies for reactions 2 and 5 by a quantity determined from the difference between the calculated and the experimental reaction enthalpies for reaction 3. After applying this shift the reaction enthalpies obtained with the CCSD(T) method were in good agreement with experiment, but also the less accurate MP2 method gave quite satisfactory results.

The lack of experimental data for Np and Pu precludes a direct calibration to experiment. One alternative would be to carry out an elaborate calculation on, for example, reaction 3, which then must give close to experimental accuracy. Both the Np and Pu complexes have, in contrast to the U complexes, open f-shells in the ground state, one for Np and two for Pu, and for Pu this implies that the ground states must be described by more than one determinant. The number of electrons that

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must be correlated in these complexes makes it necessary to use size-consistent methods, but unfortunately there are none available for the purpose at reasonable cost. CCSD(T), being a single-determinant method, cannot be applied for the Pu complexes (although it can be used on Np since only one determinant is needed to describe the ground state of single open-shell systems).

In the present study we have used the CCSD(T) method on U and Np, with different basis sets, and the CASPT2 method with a minimal reference space on Pu (4 active orbitals). For comparative purposes we also carried out MP2 and CASPT2 calculations (with a single-determinant CASSCF wave function) on the U and Np systems.

At the CCSD(T) level it was possible to use the same calibration factor for the neptunium as for the uranium complexes; the transferability of the shift was investigated by performing the calculations with large basis sets. This improved the agreement with experiment significantly for the uranium reactions, and the correlation effects turned out to be very similar for the uranium and the neptunium reactions.

The reaction energies for the Pu complexes were only obtained at the "minimal" CASPT2 level. Effective Core Potentials (ECP's) were used to remove the cores, but some irregularities in the results prompted us to investigate the effect of using ECPs at the MP2 and CASPT2 levels. The ECP effect was moderate, but not negligible, and in the final analyses we used all-electron results at the CASPT2 level for Pu. No correction factor was used in this case.

2. Theoretical Background and Computational Details

To calculate reaction enthalpies we need accurate total energies and thermodynamic functions for the reactants and the reaction products in reactions 1−5.

Total energies were obtained by using both second-order perturbation theory, MP2[4] for the closed shell uranium complexes and CASPT2[5,6] with a minimal reference space for neptunium and plutonium. In addition, the accurate coupled cluster method CCSD(T) was used for the uranium and neptunium complexes. For the closed-shell uranium compounds we used the non-iterative triples scheme suggested by Raghavachari et al.,[6] whereas the scheme suggested by Watts et al.[7] was used for the open-shell neptunium compounds.

An estimate of the rotational and vibrational contributions to the entropy and heat capacity, needed to obtain reaction enthalpies, requires reasonably accurate geometries and vibrational frequencies. Experience from the uranium systems[1] shows that geometries and vibrational frequencies calculated at the SCF level suffice for this purpose; one reason is that the lower frequencies which are reasonably well described at the SCF level dominate the contribution to the entropy at temperatures up to 1000−1500 K.

The program package Molcas5[8] was used throughout. A special purpose program was written to obtain the thermodynamic functions.

Calculations were done both at the ECP and at the all-electron level. ECPs of the Stuttgart type[9] were used in the ECP calculations. The small core ECPs suggested in ref 10 were used for the actinides, and the oxygen and the fluorine atoms were described by the energy-consistent ECPs suggested in ref 11.

Geometries were optimized at the SCF level by using ECPs and gradient techniques, in some cases with symmetry constrains. Vibrational frequencies were calculated by using the seminumerical procedure in Molcas. Correlation effects at the MP2 and CCSD(T) levels were obtained by single-point calculations at the geometry optimized at the SCF level. The 5s, 5p, and 5d shells of uranium were kept frozen in the correlation calculations.

TABLE 1: Optimized Geometry for MO_2F_2 at the SCF Level[a]

M	M−O	M−F	OMO angle	FMF angle
U	1.712	2.094	171.1	120.7
Np	1.672	2.085	174.7	133.4
Pu	1.666	2.076	174.1	117.5

[a] Distances in Å; angles in deg.

At the ECP level energies were calculated by using the standard ECP basis set from ref 10 with two polarizing *g*-functions for the actinides. For oxygen and fluorine we used two different basis sets: the standard Dolg ECP basis sets from the MOLCAS library, with a diffuse p-function and a polarizing d-function, and the ANO-L basis sets from the Molcas libraries, with 4s, 3p, 3d, and 1f ANOs. Similarly we used two basis sets for hydrogen, one with 5s functions contracted to 3s, suggested Huzinaga,[12] with a polarizing p-function added, and the 3s, 2p, and 1d ANO basis set from the Molcas libraries. The geometry optimizations were done with the smaller basis sets, omitting the diffuse p-function on hydrogen.

Basis set superposition errors were negligible, 3.7 and 3.5 kJ/mol for UF_6 and UO_3, and 6.5 and 4.3 kJ/mol for PuF_6 and PuO_3, at the MP2/CASPT2 level with use of the small basis sets.

The basis sets used in the all-electron calculations were for the actinides with 24s, 17p, 13d, and 10f basis sets optimized at the nonrelativistic level by Faegri,[13] complemented with two diffuse p-functions, one diffuse d-function, and one diffuse f-function. This basis was contracted to 9s, 8p, 7d, and 5f basis functions. For oxygen and fluorine the 9s, 5p basis of Huzinaga,[12] with the addition of one diffuse p- and one d-function, contracted to 3s, 4p, and 1d. The contraction coefficients were generated by relativistic atomic calculations. Scalar relativistic effects were included in the calculations by using the Douglas-Kroll[14] operator included in the MOLCAS package.

Spin−orbit effects were calculated for the Np and Pu complexes, which both have open f-shells in the ground state (1 for Np and 2 for Pu). The spin−orbit calculations were done by using the variation-perturbation method in the LS coupling scheme and the mean-field approximation as described in ref 11. The spin−orbit integrals were calculated with use of the AMFI[16] program as well as the recently implemented [17] approach from ref 15 and the SO-matrix elements and eigenstates were obtained with the SO-RASSI module, all of them now part of the Molcas program package. All doublet states (Np) and all singlet and triplet states (Pu) derived from the f-multiplet where included in the SO calculation. The calculated spin−orbit correction was then simply added to the ground-state total energies.

3. Results and Discussion

3.1. The Complexes. In this section we compare the different actinide complexes. The geometries and frequencies for the uranium complexes, from ref 1, were obtained without *g*-functions on the actinide.

3.1.1. MO_2F_2. The geometries, optimized at the SCF level, are shown in Table 1, and the frequencies in Table 2. The bond distances follow the expected trend, getting shorter with higher nuclear charge on the actinide. The F−M−F bond angle first increases somewhat between uranium and neptunium, and then decreases for plutonium. This may indicate a somewhat more

TABLE 2: Harmonic Frequencies Calculated at the SCF Level for MO_2F_2(g)

M	frequencies (cm)$^{-1}$
U	89.58, 219.31, 251.25, 278.10, 314.47, 549.96, 557.33, 1053.42, 1106.09
Np	70.85, 220.47, 226.6, 319.65, 350.52, 500.79, 549.98, 1101.79, 1151.29
Pu	103.96, 227.35, 266.38, 344.79, 375.63, 546.93, 555.98, 1084.66, 1155.9

TABLE 3: Geometrical Parameters for $MO_2(OH)_2$ Obtained at the SCF Level, without a p-Function on H (see text)

M	r(M-O$_{\text{uranyl}}$)	r(M-O$_{\text{hydr}}$)	Λ(O$_{\text{hydr}}$-M-O$_{\text{hydr}}$)	Λ(O$_{\text{uranyl}}$-M-O$_{\text{uranyl}}$)
U	1.73	2.13	118.4	170.4
Np	1.687	2.111	115.1	172.6
Pu	1.673	2.118	115.8	173.8

[a] All distances in Å; angles in deg.

TABLE 4: Vibrational Frequencies (in cm^{-1}) for $MO_2(OH)_2$ Calculated at the SCF Level

M	frequencies
U	97.05, 220.30, 250.99, 269.12, 299.72, 494.82, 511.55, 548.26, 554.00, 571.00, 581.00, 1025.24, 1076.44, 4182.47, 4184.17
Np	110.03, 232.03, 248.94, 321.53, 335.93, 486.74, 498.28, 538.14, 549.09, 560.15, 582.96, 1064.98, 1110.61, 4227.45, 4229.62
Pu	108.59, 223.25, 259.31, 340.69, 344.44, 406.39, 441.94, 518.2, 552.12, 565.4, 582.92, 1061.89, 1129.4, 4236.54, 4240.49

TABLE 5: Geometrical Parameters for MF_6 Obtained at the SCF Level, without a p-Function on H for U (see text)[a]

M	symmetry	r(M−F)	Hay and Martin[21]	exp
U	O_h	1.982	1.984	1.999
Np	O_h	1.950	1.972	1.981
Pu	none	1.943(4), 1.926(2)		1.971
	O_h	1.934		
	O_h ($^1A_{1g}$)	1.927	1.943 ($^1A_{1g}$)	

[a] All distances in Å.

efficient bonding in the plutonium complex. The frequencies change slightly, in a somewhat random manner, between uranium and neptunium. However, for plutonium most of the frequencies increase significantly, which confirms that the bonds are stronger in PuO_2F_2 than in UO_2F_2 and in NpO_2F_2

3.1.2. $MO_2(OH)_2$. The bond distances are slightly shorter in $NpO_2(OH)_2$ than in $UO_2(OH)_2$, but the effect is minor (Table 3). Similarly the angles vary only a little, and the changes in the vibrational frequencies (Table 4) are likewise minor.

3.1.3. MF_6. The MF_6 compounds show an expected behavior with shorter bonds and slightly higher vibrational frequencies from U to Pu (Table 5). The largest changes occur between U and Np, but since the uranium results are taken from ref 1 where no *g*-functions were included in the uranium basis set it is not clear if these differences are significant. The most striking difference between the compounds is that PuF_6 is no longer octahedral. The ground state of PuF_6 has an f ^{2} configuration corresponding to $^3T_{1g}$ ($t_{2u}{}^1$ $a_{2u}{}^1$) in the octahedral point group. This configuration will be distorted along an e_g mode, to a $^3A_{2g}$ ($b_{1u}{}^1$ $b_{2u}{}^1$) state in D_{4h} symmetry.[18] The e_g mode splits the t_{2u} orbital into an e_u and a b_{2u} orbital while the a_{2u} orbital becomes b_{1u}. The $^3A_{2g}$ state is nondegenerate and will thus not distort further by the Jahn−Teller effect. The energy lowering is small, 2 kJ/mol. However, when the symmetry is completely relaxed the system distorts further. The geometrical distortions are minor, 1−2° in the angles and 0.02 Å in the distances along the 4-fold axis, but the energy lowering is significant, 30 kJ/mol at the SCF level. This energy lowering is due to a localization effect involving the second open f-shell. The first singly occupied 5f orbital is of a_{2u} symmetry in the O_h group, where there is no interaction between the F and the Pu orbitals, while the second occupied 5f orbital has an overlap with the fluorine p orbitals. This gives rise to a symmetry breaking (which can be interpreted as a slight localization) that is responsible for the energy lowering. The reason for the symmetry breaking is a near degeneracy between the $^3A_{2g}$ ($b_{1u}{}^1$ $b_{2u}{}^1$) ground state and the excited $^3A_{2g}(e_u{}^2)$ state. When these two states are allowed to interact at the CAS level the energy is lowered by 27 kJ/mol, very close to the energy obtained when the system is allowed break symmetry at the SCF level. The mechanism is similar to the symmetry breaking in, for example, the 1s hole state in O_2.[19,20]

The geometries and vibrational frequencies of the MF_6 systems with M = U, Np, and Pu have been calculated previously by Hay et al.[21] and by Gagliardi et al.[22] The hexafluorides have been extensively studied experimentally: see for example the review by Weinstock and Goodman.[23] Vibrational spectra have been published by McDowell et al.,[24] Paine et al.,[25] Persson et al.,[26] Mulford et al.,[27] and Dewey et al.[28] Hay et al. used SCF and several DFT methods in their study, but we have only included the SCF results in Tables 5 and 6. Our bond distances are somewhat shorter than those obtained by Hay et al., probably due to the larger basis sets used in the present study. For the plutonium hexafluoride Hay et al. calculated both the geometry and the frequencies for a closed shell singlet state with a doubly occupied f^{ϕ} orbital of a_{2u} symmetry; this state is totally symmetric with no Jahn−Teller distortions. Our vibrational frequencies (Table 6) are in general lower than those of Hay et al., and in somewhat better agreement with experiment, but the differences are minor except for the E_g vibration: we calculate 423 cm^{-1} while the experimental value is 523 cm^{-1}. This is most likely an artifact of the localization. It was not possible to calculate the vibrational spectrum with the two-configuration wave function in D_{4h} symmetry. A partial frequency calculation, where the wave function was constrained to D_{2h} symmetry, gave an (averaged) E_g vibration frequency of 507 cm^{-1}.

We have also calculated the vibrational frequencies for the same closed shell singlet as used by Hay et al. (Table 6). With this constraint the E_g frequency is improved compared to the experiment, confirming that the low value obtained in the localized calculation is an artifact. The remaining frequencies change marginally, in general away from the experimental results.

3.1.4. MO_3. Also in the UO_3 system the bond lengths are getting shorter with increasing nuclear charge, with the largest decrease between uranium and neptunium (Table 7). The differences in the angles are insignificant. The bending frequencies (see Table 8) increase somewhat when going to the heavier actinides, while the variations in the stretching frequencies are minor. It seems that the bonding in MO_3 is quite similar for all three actinides.

3.2. Energies and Enthalpies of Reaction. The calculated reaction enthalpy $\Delta_r H_m°$ at 298.15 K is obtained as the difference between the total energies (at 0 K) and the thermal functions of the products and the reactants at 298.15 K including ZPE (zero-point vibration energy) correction.[29] The thermal function $H(T)$ includes the translation energy and is defined, for a given complex, as the sum of the translation, rotation, and vibration contributions at temperature T (see ref 29). The

TABLE 6: Vibrational Frequencies (in cm^{-1}) for MF_6(g) Calculated at the SCF Level[a]

M	symmetry	calculation	frequencies
U	O_h	present	**142 (T_{2u}), 196 (T_{1u}), 219 (T_{2g}), 550 (E_g), 662 (T_{1u}), 740 (A_{1g})**
		Hay[21]	157 (T_{2u}), 209 (T_{1u}), 216 (T_{2g}), 582 (E_g), 702 (T_{1u}), 761 (A_{1g})
		exp[23]	140 (T_{2u}), 184 (T_{1u}), 201 (T_{2g}), 535 (E_g), 624 (T_{1u}), 667 (A_{1g})
Np	O_h	present	**172 (T_{2u}), 214 (T_{1u}), 236 (T_{2g}), 533 (E_g), 667 (T_{1u}), 749 (A_{1g})**
		Hay[21]	180 (T_{2u}), 221 (T_{1u}), 228 (T_{2g}), 590 (E_g), 700 (T_{1u}), 711 (A_{1g})
		exp[23]	165 (T_{2u}), 195 (T_{1u}), 205 (T_{2g}), 530 (E_g), 624 (T_{1u}), 650 (A_{1g})
Pu	none	present	**177.57, 178.62, 181.74, 217.39, 222.82, 226.84, 227.41, 229.65, 235.89, 409.26, 436.95, 666.51, 670.13, 687.13, 743.2**
	O_h	present (averaged)	**180 (T_{2u}), 222 (T_{1u}), 231 (T_{2g}), 423 (E_g), 675 (T_{1u}), 743 (A_{1g})**
		present ($^1A_{1g}$)	198 (T_{2u}), 232 (T_{1u}), 250 (T_{2g}), 519 (E_g), 676 (T_{1u}), 749 (A_{1g})
		Hay[21] ($^1A_{1g}$)	203 (T_{2u}), 238 (T_{1u}), 249 (T_{2g}), 573 (E_g), 714 (T_{1u}), 759 (A_{1g})
		exp[23]	173 (T_{2u}), 203 (T_{1u}), 211 (T_{2g}), 523 (E_g), 616 (T_{1u}), 628 (A_{1g})

[a] The frequencies are averaged over symmetry components.

TABLE 7: Geometrical Parameters for MO_3 Obtained at the SCF Level, without a p-Function on H (see text)[a]

M	r(M-O$_{axial}$)	r(M-O$_{equat.}$)	Λ(O$_{axial}$-M-O$_{axial}$)	Λ(O$_{equat}$-M-O$_{axial}$)
U	1.745	1.828	165.2	97.4
Np	1.710	1.796	168.6	95.7
Pu	1.693	1.808	170.0	95.0

[a] All distances in Å; angles in deg.

TABLE 8: Vibrational Frequencies (in cm^{-1}) for MO_3(g) Calculated at the SCF Level

M	set of frequencies
U	215, 264, 272 (bending), 836 998, 1009 (stretching)
Np	240.3, 278.12, 327.68 (bending), 859.86, 1032.5, 1044.86 (stretching)
Pu	299.7, 316.29, 56.23 (bending), 835.08, 1031.92, 1052.87 (stretching)

theoretical values for $H(T)$ are obtained from calculated geometries and frequencies. The entropy, heat capacity, and thermal function $H(T)$ are shown in Table S1.

The data labeled experimental in ref 1 were derived from a combination of experiments and theory, where the latter provides information on the molecular partition function. The uncertainties in the energies of formation vary from 2 kJ/mol for UF_6(g), about 15 kJ/mol for UO_2F_2(g) and UO_3(g), to at least 25 kJ/mol for $UO_2(OH)_2$(g). In ref 1 reaction energies for reactions 1−5, with M = U, were calculated by using the same type of basis sets as in the present study, but without *g*-functions on U. At the CCSD(T) level the results were very close to experiment for all reactions not involving HF, but poor as soon as HF appeared among the reaction products. The error appeared to be associated with different errors in the description of the ionic bonds in the uranium(VI) complexes and in HF; this systematic error could be almost completely removed by calibrating to one of the reactions involving HF. The calibrated results were of fair to good accuracy also at the MP2 and the B3LYP levels. The results from ref 1 are summarized in Table 9.

No experimental data are available for the higher actinides, and thus the same calibration procedure cannot be used directly. One theoretical possibility would be to carry out calculations to experimental accuracy, but this would be exceedingly difficult, if not impossible. However, if the same quality basis sets are used along the series U−Np−Pu, it is reasonable to assume that the relative errors between the HF bond and the M−F, M−O, and M−OH bonds are similar for M = Np and Pu as for M = U, which would allow us to use the calibration of the uranium reaction enthalpies also for Np and Pu. The error involved in this procedure assessed by comparing results obtained with larger basis sets at the CCSD(T) level for U and Np (CCSD(T) cannot be used for Pu due to the multireference character of the states in a f^2 system).

Two different basis sets were used in the investigation: the original basis from ref 1 but with two diffuse *g*-functions added to the actinide basis, and one in which the ANO-L basis sets from the Molcas library were used on F and O.

3.2.1. Uranium. The results obtained for the uranium complexes together with the corresponding small basis set results from ref 1 are shown in Table 10.

Let us first consider reactions 1 and 4, which do not involve HF. The effect, at the CCSD(T) level, of increasing the basis set is small for reaction 1, as expected since it does not contain HF. However, the effect on reaction 4 is larger. The effect of adding the *g*-functions to uranium is to make the reaction less exothermic, by 14 kJ/mol, while the effect of using the ANO-L basis on the lighter atoms is to restore the value obtained with the small basis without *g*-functions. This result indicates that adding *g*-functions to the actinide center in the small basis set calculations induces a certain basis set imbalance favoring the U−O bond over the U−OH bond. Turning to reactions 2, 3, and 5 which all have HF at the right-hand side in the reaction, the error per HF molecule relative to "experiment" in the small basis without *g*-functions is 23 kJ/mol for reaction 2, 19 kJ/mol for reaction 4, and 21 kJ/mol for reaction 5. The corresponding numbers for the large ANO-L basis set are 11, 8, and 10 kJ/mol. The error decreases with the size of the basis set, as expected, and it scales well with the number of HF molecules involved. For the small basis set with *g*-functions on the actinide, the error per HF is 14 and 15 kJ/mol for reactions 3 and 5, but 24 kJ/mol per HF for reaction 2. In both reactions 2 and 4, $UO_2(OH)_2$ appears as a reaction product. The results for reaction 4 showed an imbalance where the $UO_2(OH)_2$ complex was less well described than the UO_3 complex, by about 15 kJ/mol. If this error would be similar for reaction 2 (recall that the basis set effect was negligible in reaction 1) we should subtract this value from the reaction energy, which would give a remaining error for reaction 2 of 33 kJ/mol or about 16 kJ/mol per HF, in agreement with the errors obtained for reactions 3 and 5. The conclusion is that the addition of *g*-functions to the actinide when the small basis set is used for O and F results in an imbalance and is due to the small basis set with *g*-functions that is of the order of 15 kJ/mol at the CCSD(T) level.

The shift used in ref 1 was calculated from the difference between theory and experiment for reaction 3 for uranium. In the old basis set the shift, at the CCSD(T) level, was 19.0 kJ/mol per HF. Similarly, the shifts for the small basis set with *g*-functions and for the large ANO-L basis sets at the CCSD(T) level are 13.5 and 7.75 kJ/mol, respectively. The shifted CCSD(T) results are shown in Table 11. At this level of approximation, the estimated reaction enthalpies obtained with the old basis set and the large ANO-L basis set are almost identical. However, the small basis set with *g*-functions gives

TABLE 9: Previous Gas-Phase Results for the Reaction Enthalpy from Ref 1[a]

	$2UO_3 + UF_6 \rightarrow 3UO_2F_2$	$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	$\mathbf{UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF}$	$UO_3 + H_2O \rightarrow UO_2(OH)_2$	$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$
SCF	−567 (257)	131 (66)	170 (17)	−237 (53)	539 (104)
MP2	−278 (32)	101/79 (36/14)	232/187 (45/0)	−154 (30)	487/419 (51/16)
CCSD(T)	−329 (18)	110/72 (46/7)	263/187 (76/0)	−186 (2)	558/444 (123/9)
B3LYP	−262 (49)	130/58 (65/6)	332/187 (145/0)	−166 (18)	627/411 (192/24)
exp	−311	65	187	−184	435

[a] Corrected values (see text) are given after the slash for reactions 2, 3, and 5. Numbers in parentheses are deviations from experiment.

TABLE 10: Results for the Reaction Enthalpy with *g*-Functions in the Basis Set of Uranium[a]

reaction	$2UO_3 + UF_6 \rightarrow 3UO_2F_2$	$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	$\mathbf{UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF}$	$UO_3 + H_2O \rightarrow UO_2(OH)_2$	$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$
MP2 from ref 1	−278 (−32)	101 (−36)	**232 (−45)**	−154 (−30)	487 (−51)
MP2 S.B.,	−288 (−23)	105 (−40)	**200 (−13)**	−139 (−45)	443 (−8)
MP2 all-electron S.B.	−306 (−5)	86 (−21)	**168 (19)**	−151 (−33)	405 (30)
CCSD(T) from ref 1	−329 (18)	110 (−46)	**263 (−76)**	−186 (2)	558 (−123)
CCSD(T) small basis	−329 (18)	113 (−48)	**241 (−54)**	−172 (−12)[b]	526.3 (−91)
CCSD(T) ANO-L basis	−332 (21)	87 (−22)	**218 (−31)**	−188 (3.5)	492 (−57)
exp	−311	65	**187**	−184	435

[a] In the present calculations *g*-functions are included in the uranium basis, but no *g*-functions were used in ref 1. Energies in kJ/mol. The numbers in parentheses are the absolute deviations from the experimental enthalpies. [b] Observe the different sign of the error for the basis set with *g*-functions.

TABLE 11: Shifted CCSD(T) Reaction Enthalpies for Uranium[a]

reaction	$2UO_3 + UF_6 \rightarrow 3UO_2F_2$	$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	$\mathbf{UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF}$	$UO_3 + H_2O \rightarrow UO_2(OH)_2$	$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$
from ref 1	−329 (18)	72 (−7)	**187 (0)**	−186 (2)	444 (−9)
small basis	−329 (18)	83 (−12)	**187 (0)**	−172 (−12)[b]	445 (−10)
ANO-L basis	−332 (21)	72 (−7)	**187 (0)**	−188 (4)[b]	446 (−11)
exp	−311	65	**187**	−184	435

[a] The procedure is explained in the text. Energies in kJ/mol. The difference relative to experiment is given in parentheses. [b] Observe the different sign of the error for the basis set with *g*-functions.

somewhat less accurate results due to the basis set imbalance discussed above. At this level of accuracy we thus have an uncertainty, due to the basis set, of about 15 kJ/mol.

At the MP2 level the results are less accurate, as discussed in ref 1. The error in the corrected reaction enthalpies with the old basis set is about 30 kJ/mol for reactions 1 and 4, which do not involve HF, and it is smaller for reactions 2 and 5 (however, it should be noted that while the reaction enthalpy is underestimated for reaction 1 at the MP2 level it is overestimated at the CCSD(T) level). When two *g*-functions are added to the basis set the error increases for reaction 2 from 14 to 33 kJ/mol and for reaction 4 from 30 to 45 kJ/mol. The same imbalance that was found at the CCSD(T) level thus occurs also in the MP2 calculations. The MP2 results are in general of lower quality than the CCSD(T) results. The errors in the reactions involving HF do not scale as well as they did at the CCSD(T) level, in particular in the present calculations with *g*-functions in the uranium basis.

The molecular orbitals at the ECP level are nodeless in the core region, and this may have some effects in particular at the MP2 level. To get a measure of this error we also carried out MP2 calculations at the all-electron level. The results are shown in Table 10. For the uranium complexes the MP2 error that can be associated directly with the ECP is sizable, ranging from 12 kJ/mol for reaction 4 to 39 kJ/mol for reaction 5. As at the ECP level, the error compared to experiment does not scale very well with the number of HF in reactions 2, 3, and 5 and a correction procedure does not seem appropriate. The all-electron mean deviation, σ_n, is 10 kJ/mol, which is slightly smaller than the ECP mean deviation, 13 kJ/mol. The largest error, 33 kJ/mol, occurs for reaction 4, and the uncertainty in the calculated reaction enthalpies at the all-electron level can be estimated as 30−40 kJ/mol and thus about 10 kJ/mol larger at the ECP level. The source of this problem is probably connected with the overlap between the diffuse un-contracted basis functions in the ECP basis sets and the nodeless occupied orbitals.

Finally, one should note that the stoichiometric coefficient for the uranium(VI) products is different in reactions 1−5. The large correlation effect in reaction 1, as well as the large difference between the MP2 and the CCSD(T) results, should therefore be divided by three to be comparable with the corresponding values for reactions 2−5. When this is done the result becomes comparable for all reactions.

3.2.2. Neptunium. For Np, with one open f-shell, only the basis sets with *g*-functions on Np were used. The results are shown in Table 12. At the CCSD(T) level the basis set effect in going to the large ANO-L basis is 8, 23, 24, 16, and 32 kJ/mol compared to 3, 26, 23, 15, and 34 kJ/mol for uranium. The basis set effect is thus very similar for both elements, and it is reasonable to assume that this would be the case also when using larger basis sets. The very large basis set reproduces the “experimental” results for uranium rather well, and considering the agreement between the basis set effects for U and Np, we conclude that the same correction can be used for Np as for U.

The corrected neptunium CCSD(T) results are shown in Table 13, together with the calculated spin−orbit correction. Also included in the table are the uncorrected all-electron MP2 results. The corrected CCSD(T) ANO-L results, corrected for the spin−orbit interaction, provide our best estimates for the reaction enthalpies for the neptunium reactions. By comparison with the deviations from the experimental results for the uranium reactions, Table 11, we estimate the error in the estimated neptunium reaction enthalpies at about 20 kJ/mol.

TABLE 12: Unshifted Results for Np (in kJ/mol)[a]

reaction	$2NpO_3 + NpF_6 \rightarrow 3NpO_2F_2$	$NpO_2F_2 + 2H_2O \rightarrow NpO_2(OH)_2 + 2HF$	$NpF_6 + 2H_2O \rightarrow NpO_2F_2 + 4HF$	$NpO_3 + H_2O \rightarrow NpO_2(OH)_2$	$NpF_6 + 3H_2O \rightarrow NpO_3 + 6HF$
CASPT2 ECP, S.B.[b]	−236 (−14)	90 (19)	180 (−22)	−118 (1)	387 (−38)
CASPT2 AE, S.B.	−222	71	158	−119	349
CCSD(T) S.B.	−287	97	215	−154	466
CCSD(T) ANO-L	−295	74	191	−170	434

[a] Reaction enthalpies within the MP2 and CCSD(T) level. S.B. stands for small basis with a *g*-function added to Np. ANO-L stands for large ANO basis (see text). SOC stands for spin−orbit coupling effect. [b] The numbers in parentheses are the differences between the ECP and the all-electron reaction enthalpies at the MP2 level.

TABLE 13: CCSD(T) and All-Electron CASPT2 Reaction Enthalpies for Np, with the Uranium Shift Applied for Reactions 2, 3, and 5 for the CCSD(T) Results[a]

reaction	$2NpO_3 + NpF_6 \rightarrow 3NpO_2F_2$	$NpO_2F_2 + 2H_2O \rightarrow NpO_2(OH)_2 + 2HF$	$NpF_6 + 2H_2O \rightarrow NpO_2F_2 + 4HF$	$NpO_3 + H_2O \rightarrow NpO_2(OH)_2$	$NpF_6 + 3H_2O \rightarrow NpO_3 + 6HF$
CASPT2 all electron	−222 (73)[b]	71 (13)[b]	158 (−2)[b]	−119 (51)[b]	349 (−39)[b]
CASPT2 all electron with SOC	−232	66	158	−131	354
CCSD(T) S.B.	−287	70	161	−154	385
CCSD(T) ANO-L	−295	58	160	−170	388
CCSD(T) S.B. with SOC	−297	63	161	−166	390
CCSD(T) ANO-L with SOC	−305	51	160	−182	393
SOC S.B.	−10.3	−6.7	−0.3	−11.7	4.8

[a] Energies in kJ/mol. S.B stands for small basis with a *g*-function added to Np. ANO-L stands for large ANO basis (see text). SOC stands for spin−orbit coupling effect. [b] Difference between the CASPT2 and the CCSD(T)/ANO-L results.

TABLE 14: Results for Pu Small Basis Set Including *g*-Functions on Pu[a]

	$2PuO_3 + PuF_6 \rightarrow 3PuO_2F_2$	$PuO_2F_2 + 2H_2O \rightarrow PuO_2(OH)_2 + 2HF$	$PuF_6 + 2H_2O \rightarrow PuO_2F_2 + 4HF$	$PuO_3 + H_2O \rightarrow PuO_2(OH)_2$	$PuF_6 + 3H_2O \rightarrow PuO_3 + 6HF$
CASPT2 ECP	−446	108	23	−126	257
CASPT2 all-electron	−455	90	−4	−136	222
CASPT2 all-electron with SOC	−438	95	11	−130	236
SOC	17	5	15	6	14

[a] SOC is the calculated spin−orbit correction. The energies are given in kJ/mol.

TABLE 15: Summary of Spin-Free Reaction Enthalpies at the All-Electron MP2/CASPT2 Level

M	$2MO_3 + MF_6 \rightarrow 3MO_2F_2$	$MO_2F_2 + 2H_2O \rightarrow MO_2(OH)_2 + 2HF$	$MF_6 + 2H_2O \rightarrow MO_2F_2 + 4HF$	$MO_3 + H_2O \rightarrow MO_2(OH)_2$	$MF_6 + 3H_2O \rightarrow MO_3 + 6HF$
U	−306	86	168	−151	405
Np	−222	71	158	−119	349
Pu	−455	90	−4	−136	222

By comparing the results obtained with the CCSD(T) and the one reference CASPT2 method we can estimate errors in reaction enthalpies calculated at the CASPT2 level. The ECP and the all-electron CASPT2 results are shown in Table 12. The errors in the ECP reaction enthalpies, compared to the all-electron results, are similar to those found for uranium. As discussed in connection with the uranium reactions, the MP2 results do not scale well with the number of HF molecules in reactions 2, 3, and 5, and it is not meaningful to correct the CASPT2 energies for neptunium. Table 13 shows, within parentheses, the differences between the un-corrected all-electron MP2 results and the corrected result obtained in the CCSD(T) ANO-L calculations. This difference is large for reaction 1, 73 kJ/mol. For reactions 4 and 5 the difference is also sizable, 51 and 39 kJ/mol, but of the same order as for the corresponding uranium reactions, 33 and 41 kJ/mol. For uranium, the reaction exothermicity for reaction 1 is overestimated in the CCSD(T) ANO-L calculation by 20 kJ/mol. Taking this into consideration, we can estimate the error in the reaction obtained at the all-electron MP2 level for neptunium at about 50 kJ/mol.

In reaction 1, there are three complexes involved in the reaction, and to compare the difference between the MP2 and the CCSD(T) results with the other reactions with only one uranium complex involved we should thus divide the difference by 3. The “normalized” difference is then close to that obtained for a reaction involving one actinide, 24 kJ/mol.

3.2.3. Plutonium. Due to the multireference character of the wave functions for the plutonium compounds it is no longer possible to use the CCSD(T) method. DFT-based methods are presently excluded for the same reason. Alternatives, such as full valence CASPT2, cannot be used either due to the large active space needed for an accurate description of the systems. The large number of electrons which need to be correlated also preclude the use of multireference SDCI-type methods since the size-consistency error becomes too large. The best alternative is thus to use minimal reference CASPT2, which should be of the same quality as MP2 for uranium, and to try to use the results obtained for uranium and neptunium to estimate the error in the calculated reaction enthalpies.

The reaction enthalpies calculated at the CASPT2 level are shown in Table 14. The difference between the ECP and the all-electron results are similar to those found for uranium and neptunium. At the CASPT2 level it appears that the all-electron results are somewhat more reliable than the ECP results. Our best estimate of the reaction enthalpies is thus provided by the spin−orbit corrected all-electron CASPT2 results, shown in the last row in Table 14. Using the results for neptunium, we estimate the error in the calculated reaction enthalpies at about 50 kJ/mol.

3.2.4. A Comparison of the Reaction Enthalpies. The reaction enthalpies at the MP2/CASPT2 level are summarized in Table 15. For U and Np the reaction enthalpies are reasonably similar: for reactions 2, 3, and 4 the difference is about 30 kJ/mol or less, and for reactions 1 and 5 the difference is about 60−80 kJ/mol. Similarly, the reaction enthalpies for plutonium for reactions 2 and 4 are reasonably similar to the corresponding reaction enthalpies for U and Np.

However, the plutonium results differ markedly from those obtained for U and Np for reactions 1, 3, and 5. Comparing with Np, reaction 1 is much more exothermic (by more than 230 kJ/mol) and reactions 3 and 5 are much less endothermic (about 160 and 130 kJ/mol, respectively). The differences are significant even allowing for the fairly high error associated with the MP2 method. One common feature of reactions 1, 3, and 5 is that MF_6 is one of the reactants. It thus seems reasonable to assume that the difference is associated with weaker bonding in PuF_6 (relative to the other Pu compounds) compared to uranium and neptunium. This is most certainly due to the f-shell occupation in PuF_6. The first f-electron enters, as for Np, a noninteracting a_{2u} orbital. The second f-electron enters a higher degenerate t_{2u} orbital that interacts with one of the fluorine p-orbital combinations which has two consequences. First, since the f-orbital mixes with the fluorine p-orbitals it becomes antibonding between Pu and F (the bonding combination is the doubly occupied orbital localized largely on fluorine). This will raise the energy of the 5f-orbital. Second, the occupation of an f-orbital that interacts with the p-orbitals on F will decrease the availability of f-orbitals for the bonding. The total f-populations on U, Np, and Pu in the MF_6 molecules are 1.5, 2.7, and 3.3, which shows that the f-admixture in the bonding orbitals has decreased in Pu relative to U and Np. This indicates that the second effect probably dominates for the weakening of the bond. The effect of occupying a second f-orbital will be smaller for the other complexes, since there is a larger freedom to adjust due to the lower symmetry.

4. Conclusions

On the basis of our previous calculations of the reaction enthalpies of reactions 1−5 for uranium(VI), we have calculated the reaction enthalpies also for neptunium(VI) and plutonium(VI). The reaction enthalpies for the neptunium reactions were calculated at the CCSD(T) level with different basis sets, while only MP2 was used for plutonium. We estimate the uncertainty in the reaction enthalpies for the neptunium reactions at about 20 kJ/mol, and that for the plutonium reactions at about 50 kJ/mol. We also have found that the error in the reaction enthalpies calculated at the MP2 or minimal CASPT2 level using ECPs is sizable.

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Supporting Information Available: The entropy, the heat capacity, and the thermal function $H(T)$ for the Np and Pu compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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