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Structure and Thermodynamics of Uranium(VI) Complexes in the Gas Phase: A Comparison of Experimental and ab Initio Data

Timofei Privalov,† Bernd Schimmelpfennig,‡ Ulf Wahlgren,*,† and Ingmar Grenthe§

Department of Physics, AlbaNova University Center, Stockholm University, S-106 91 Stockholm, Sweden, Theoretical Chemistry, Department of Biotechnology, AlbaNova University Center, The Royal Institute of Technology, S-106 91 Stockholm, and Inorganic Chemistry, Department of Chemistry, The Royal Institute of Technology, Teknikringen 30, S-10044 Stockholm, Sweden

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Ab initio methods were applied for the calculation of the total energy and the molar entropy and heat capacity of the compounds UO_2F_2, $UO_2(OH)_2$, UF_6, and UO_3 in the gas phase with the purpose to obtain thermodynamic data for reactions that can be compared with experimental values. The total energy, geometry, and vibration frequencies were calculated at different levels of accuracy: second-order perturbation theory (MP2), coupled cluster theory (CCSD(T)), and density functional theory (B3LYP). Our results agree well with experimental values and previous theoretical results. Additionally, the transition state of UO_2F_2(g) was studied and the value of the barrier for the inversion of the fluoride atoms was calculated.

1. Introduction

In a previous study we have investigated the structures and relative stability of hydroxide and fluoride complexes of UO_2^{2+} in the gas phase and different solvent models using quantum chemical methods; the theory-based data were in close agreement with experimental structure information.[1] It is well-known that quantum chemical estimates on the thermodynamics of chemical reactions in solution are not very precise,[2] but the situation may well be different for reactions between gaseous uncharged species. However, there is very little experimental and theory-based information on reactions of this type for the actinide elements. In the present inquiry we have investigated the thermodynamics of reactions between different gaseous uranium(VI) species and explored the accuracy of different quantum chemical methods by comparison with experimental data taken from the literature. The experimental database on the thermodynamics of gaseous uranium(VI) species is limited and the accuracy of the data is not always high. This is due both to the difficulty to make investigations at high temperature and to analyze the often complex reactions. Compilations and critical evaluations of thermodynamic data, S°_m, $C^\circ_{p,m}$, $\Delta_f G^\circ_m$, and $\Delta_f H^\circ_m$, are given in refs 3 and 4; these data have been used to calculate the Gibbs energy and enthalpy of reaction, $\Delta_f G^\circ_m$ and $\Delta_f H^\circ_m$, which are compared with the corresponding data deduced from theory.

Gas phase reactions involving actinides are not only interesting from a modeling point of view, they 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. An important aim of the present study is to develop computational models that can be used with reasonable confidence to obtain thermodynamic data on actinide complexes when no experimental data are available, as is frequently the case for actinides other than uranium.

We have studied the following reactions and calculated the enthalpy and entropy of reaction at 298.15 K:

$$2UO_3(g) + UF_6(g) \rightarrow 3UO_2F_2(g) \quad (1)$$

$$UO_2F_2(g) + 2H_2O(g) \rightarrow UO_2(OH)_2(g) + 2HF(g) \quad (2)$$

$$UF_6\,(g) + 2H_2O(g) \rightarrow UO_2F_2(g) + 4HF(g) \quad (3)$$

$$UO_3\,(g) + H_2O(g) \rightarrow UO_2(OH)_2(g) \quad (4)$$

$$UF_6(g) + 3H_2O\,(g) \rightarrow UO_3\,(g) + 6HF(g) \quad (5)$$

The entropy and heat capacity of reactants and products were calculated using the vibration and rotation partition functions based on accurate geometries and vibrational frequencies obtained by quantum chemical methods. Many of the previous estimates of these quantities were based on very crude geometry models (see section 2).

Most of the reactions studied involve fluoride compounds, and this represents a particular theoretical challenge due to the known difficulty to describe the fluoride ion in a balanced way with a restricted basis set. However, this turned out to be a systematic error in the thermodynamic quantities for the reactions involving hydrogen fluoride, and it was therefore possible to calibrate the results using a reference reaction (see section 3).

We demonstrate in this study that reliable thermodynamic data can be obtained by a model that combines affordable computational methods together with calibrations to data from some known reaction.

2. Theoretical Background and Computational Details

A high quality estimate of the rotational and vibrational contributions to the entropy and heat capacity requires precise geometries, these and the vibrational frequencies were calculated at the SCF level and with the hybrid density functional B3LYP. Total energies were obtained using the perturbation method MP2, the coupled cluster method CCSD(T), and density

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† Stockholm University.

‡ Department of Biotechnology, The Royal Institute of Technology.

§ Department of Chemistry, The Royal Institute of Technology.

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TABLE 1: Optimized Geometry for UO_2F_2[a]

method	state	U−O	U−F	OUO angle	FUF angle	$10^{-113}I_1I_2I_3$
SCF (M)	GS	1.712	2.094	171.1	120.7	2.159
B3LYP (G)	GS	1.772	2.072	168.52	113.56	2.258
SCF (M)	TS	1.704	2.115	180.0	180.0	1.897
estimated[14]	GS	1.80	2.00	100	120	2.21

[a] Distances in Å, angles in degress, and the product of the moments of inertia, $I_1I_2I_3$, in g^3 cm^6. Labels M and G stand for Molcas5 and Gaussian98.

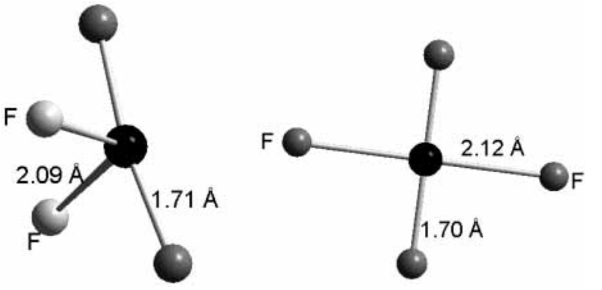

Figure 1. (Left) structure of UO_2F_2(g). (Right) transition state for the reaction where the fluoride atoms are inverted across the UO_2 unit.

functional theory (B3LYP). The calculations have been carried out using the program packages Molcas5[5] and Gaussian98.[6]

Effective core potentials (ECP) of the Stuttgart type[7] were used in all the calculations. Previous studies[8,9] have proved the accuracy of these energy consistent ECP's. The small core ECP with 32 electrons in the valence shell suggested in ref 10 was used for uranium. The oxygen and the fluorine atoms were described by the same type of energy consistent ECP's,[11] with polarizing d-functions included in the basis set, and for hydrogen we used basis set parameters suggested by Huzinaga[12] with 5s functions contracted to 3s. The geometry optimizations were made using a hydrogen basis set without a diffuse p-function, whereas a diffuse p-function with exponent 0.8 was added for the energy calculations at the correlated level.

Geometries were optimized at the SCF and B3LYP levels using gradient techniques; in some cases with symmetry constrains. Correlation effects estimated 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.

3. Results and Discussion

3.1. Properties of the Complexes. *UO_2F_2(g).* The optimized geometry of UO_2F_2 in the ground state (GS) at the SCF and B3LYP level is shown in Table 1 and in Figure 1. The optimization was done without symmetry restrictions, but the geometry converged to C_{2v} symmetry. The uranyl unit is essentially linear, with the F−U−F angle close to 120°. The complex can thus "flip" between two structures with the fluorides at opposite sides of the uranium atom; we have investigated the rate and mechanism of this reaction. The transition state, cf. Figure 1, is planar with D_{2h} symmetry.

The rate constant for the exchange is

$$k(T) = (k_B T/h)e^{-\Delta G^{\ddagger}/RT} \tag{6}$$

where

$$\Delta_r G^{\ddagger} = \Delta_r H^{\ddagger} - T\Delta_r S^{\ddagger} \tag{7}$$

TABLE 2: Harmonic Frequencies Calculated at the SCF Level for UO_2F_2(g)[a]

method	state	set of frequencies $(cm)^{-1}$
SCF (M)	GS	90, 219, 251, 278, 314, 550, 557, 1053, 1106
B3LYP (G)	GS	80, 202, 213, 220, 235, 550, 563, 896, 969
SCF (M)	TS	i77, 190, 250, 290, 350, 524, 532, 1064, 1120
ref 14	GS	150, 150, 180, 200, 200, 550, 600, 830, 850

[a] Labels M and G stand for Molcas5 and Gaussian98.

TABLE 3: Thermochemical Properties of UO_2F_2(g) [(J/mol)/K] at the Standard Conditions (T = 298.15 K)

method	S_{trans}	S_{rot}	S_{vib}	S_{tot}	$C_{p,vib}$	C_p
Molcas SCF	181	107	48	334	49	82
Gaussian B3LYP	181	107	55	343	52	85
ref 14				328		83
ref 15				342.7 ± 10		86.4 ± 5

The $\ddagger$ − quantities are the difference between the corresponding thermodynamic quantities in the ground and transition states.

The B3LYP functional gives a U−O distance 0.06 Å longer than the one obtained at the SCF level. Previous studies[1,13] have shown that the internal uranyl U−O bond is about 0.06 Å too short at the SCF level, indicating that the B3LYP provides a better agreement with experiment. However, this deficiency of the SCF approximation does not appreciably influence other properties such as reaction energies.

The barrier to inversion of the fluoride atoms in UO_2F_2 is 18 kJ/mol at the SCF level and 22 kJ/mol at the MP2 level. This corresponds to a temperature close to 2400 K. The potential surface for the inversion will therefore be far from harmonic already in the range 1000−1500 K, with progressively larger errors in all thermodynamic quantities. Our estimate suggests that the rate of inversion at room temperature is 71 s^{-1}, whereas it is much larger at 1500 K, 8.6×10^4 s^{-1}.

The calculated harmonic vibration frequencies are shown in Table 2. The frequencies ν_i obtained at the SCF and B3LYP levels are in reasonable agreement, in particular in the low energy part of the spectrum. CI effects should normally affect the higher levels more, and the deviations between the results also increase markedly at about 1000 cm^{-1}. There is only one imaginary frequency at the transition state.

Calculated thermodynamic properties at T = 298.15 K are shown in Table 3.

The agreement between the thermodynamic properties at the SCF and B3LYP levels is satisfactory at room temperature, despite the differences for the higher vibration frequencies. This is due to the small contribution of the high energy levels to the entropy and the heat capacity at room temperature. For example, the vibration contribution to the entropy is

$$S_{vib} = R\sum_{i=1}^{3N-6}\left[\Omega_i\frac{1}{e^{\Omega_i}-1} - \ln(1 - e^{-\Omega_i})\right] \tag{8}$$

where $\Omega_i = h\nu_i/k_BT$, here h is the Planck's constant, k_B is the Boltzmann constant, R is the molar gas constant, and ν_i denotes the vibration frequency of the i:th mode ($i = 1, ..., 3N - 6$). It is clear from eq 8 that at room temperature the main contributions to the entropy come from the lower frequencies.

In Table S1 we show the various contributions to the entropy and to the heat capacity at 298.15 K and at 1500 K. The latter are expected to be rather poor due to the importance of the anharmonic contributions at this high temperature.

Estimates of the entropy and heat capacity of UO_2F_2(g, 298.15 K), based on an assumed C_{2v} geometry and bond distances estimated from the known structures of the corresponding Cr,

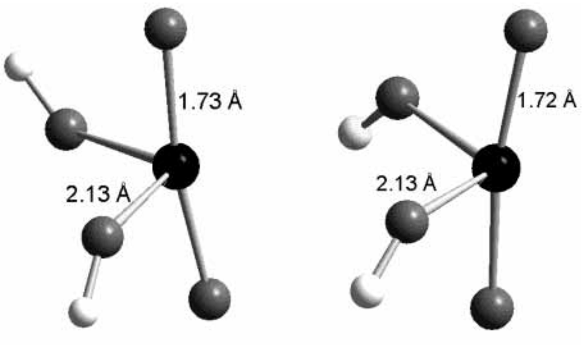

Figure 2. Structures of *trans*- and *cis*-$UO_2(OH)_2$(g).

TABLE 4: Geometrical Parameters for $UO_2(OH)_2$(g) Obtained at the SCF Level, without a p-Function on H (see Text)[a]

property	*cis*-$UO_2(OH)_2$	*trans*-$UO_2(OH)_2$
$r(U-O_{hydr})$	2.13	2.13
$\Lambda(O_{hydr}-U-O_{hydr})$	119.5	118.4
$r(U-O_{uranyl})$	1.72	1.73
$\Lambda(O_{uranyl}-U-O_{uranyl})$	170.3	170.4
total energies (SCF level)	−539.60697014	−539.60725083

[a] All distances in Å, angles in degrees, and total energies in atomic units.

TABLE 5: Vibrational Frequencies (cm^{-1}) for $UO_2(OH)_2$(g) Calculated at the SCF Level

cis isomer	98.21, 220.49, 251.04, 267.39, 299.02, 493.42, 499.18, 531.74, 560.75, 566.28, 583.25, 1023.93, 1077.81, 4184.31, 4185.98
trans isomer	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

Mo, and W compounds, have been made by Ebbinghaus[14] and by Glushko et al.[15] Both the geometry and the vibrational spectrum suggested by these authors differ appreciably from our results (estimates of the vibrational frequencies from Ebbinghouse[14] are included in Table 2). There are important differences between our geometry and those estimated in refs 14 and 15; the UO_2 unit is linear in our case, whereas it is bent, angle 100°, in the previous models. The U−O and U−F distances are rather similar, and therefore also the product of the three principal moments of inertia, which is the quantity entering the expression for the rotational entropy; our value is 2.16×10^{-113} g^3 cm^6 and that of Ebbinghaus is 2.21×10^{-113} g^3 cm^6. More surprisingly, the entropy and the heat capacities are also in reasonable agreement (see Table 3) despite the differences in vibration frequencies. The reason is presumably that the distribution of the lower frequencies, which dominate the contribution to the thermodynamic functions, is similar and that the vibrational contribution to the entropy is only 10−20% and to the heat capacity about 50% (see table S1).

$UO_2(OH)_2$(g). Two stable structures with only real vibration frequencies were identified, one (cis) with both hydroxides being bent upward from the equatorial plane and the other (trans) with one hydroxide bent up and the other down (see Figure 2).

The result of the geometry optimization is shown in Table 4. The two structures are almost degenerate and have very similar bond distances. At the SCF and MP2 levels the trans structure is marginally lower in energy than the cis structure by 0.7 and 0.9 kJ/mol, respectively. The entropy of the trans structure is slightly smaller than that of the cis structure. The calculated harmonic frequencies are shown in Table 5 for both isomers. The moments of inertia are also almost the same for the two structures: 3.5637×10^{-38}, 2.6256×10^{-38}, and 2.21445×10^{-38} g·cm^2 for the cis configuration, and 3.5637×10^{-38}, 2.6282×10^{7}, and 2.2280×10^{-38} g·cm^2 for the trans configuration. The difference in energy, vibration frequencies, and moments of inertia between the two isomers is negligible at all temperatures. Both Ebbinghaus[14] and Gorokhov and Sidorova[16] have calculated the entropy and heat capacity in C_{2v} symmetry, Gorokhov and Sidorova using estimated molecular parameters from the iso-electronic MO_2F_2(g) structures of Cr, Mo, and W. The difference between the two entropy estimates is quite large (22.5 J/(K·mol)).

TABLE 6: Entropy S and Constant Pressure Heat Capacity, C_p, for $UO_2(OH)_2$(g) at 298.15 K and 1 atm (1 bar in Ref 12)

complex	S [(J/mol)/K]	C_p [(J/mol)/K]
cis-$UO_2(OH)_2$	349.34	102.57
trans-$UO_2(OH)_2$	349.14	102.30
ref 14	370.005	100.884
ref 16	347.45	100.82

Calculated thermodynamic properties for $UO_2(OH)_2$ are shown in Table 6. The differences between the two isomers are insignificant.

TABLE 7: Vibrational Frequencies (cm^{-1}) for UF_6(g) Calculated at the SCF Level[a]

theor freq, SCF	exp freq, McDowell et al.[20]	theor freq, Hay et al.[13]		exp freq, Aldridge et al.[21]
		SCF	B3LYP	
142 (T_{2u})	143 (T_{2u})	157	150	143.0 (144)
196 T_{1u})	186 (T_{1u})	209	191	187.5 (189)
219 (T_{2g})	200 (T_{2g})	216	178	201.0 (202)
550 (E_g)	534 (540) (E_g)	582	552	534.5 (541)
662 (T_{1u})	626 (634) (T_{1u})	702	647	627.0 (636)
740 (A_{1g})	667 (672) (A_{1g})	761	653	668.2 (673)

[a] Values in parentheses refer to the experimental harmonic frequencies.

UF_6. Experimentally, uranium hexafluoride has octahedral symmetry; ab initio calculations are in exact agreement with experiment concerning the symmetry of the complex. The optimized U−F bond distance is 1.982 Å at the SCF and 2.007 Å at the B3LYP level. Previous studies report similar bond distances. Hay et al.[13] obtained 1.984 Å at the SCF level and 2.014 Å at the B3LYP level, using a large core ECP for uranium. Han[17] reports a B3LYP value of 2.007 Å. Experimental values reported by Weinstock and Goodman[18] and by Hargittai[19] are 1.999 and 1.996 Å, respectively (see also ref 22). Calculated vibrational frequencies, together with previous theoretical results from Hay and Martin, and experimental results from McDowell et al.[20] and from Aldridge et al.,[21] are shown in Table 7. There are four triple degenerate (T_{2u}, T_{1u}, T_{2g}, T_{1g}), one double degenerate mode (E_g), and one nondegenerate mode of A_{1g} symmetry. The agreement with experiment is quite good, in particular for the lower frequencies. At higher frequencies the discrepancies are larger, due to the neglect of correlation as well as anharmonic effects. However, the deviations are reasonably small also for the highest frequencies. Our results also agree well with SCF results reported by Hay et al.[13] Their B3LYP results differ from the SCF results for the higher frequencies due to the neglect of correlation in the latter calculations.

UO_3. Previous experimental studies[23−25] of matrix-isolated UO_3 provide information on the infrared spectra and geometry of uranium trioxide with different oxygen isotope substitutions. A value of 180° for the angle between the two equivalent uranium−oxygen bonds was reported for $U^{16}O_3$. The frequencies of 844, 746, and 853 cm^{-1} were reported on the basis of the spectrum of the argon-trapped $U^{16}O_3$ species. The structure data

TABLE 8: Properties of UO_3(g) Obtained at the SCF Level[a]

property	calculated values	calculated values (ref 27)
$r(U-O_{axial})$	1.745	1.81
$r(U-O_{equat})$	1.828	1.85
$\Lambda(O_{axial}-U-O_{axial})$	165.2	158.8
$\Lambda(O_{equat}-U-O_{axial})$	97.4	100.6
frequencies	215, 264, 272 (bending)	
	836 998, 1009 (stretching)	782, 885, 887
moments of inertia ($\times 10^{-38}$)	2.4773, 1.5914, 0.88557	

[a] Frequencies in cm^{-1}, moments of inertia in g·cm^2, distances in Å, and bond angles in degrees.

TABLE 9: Thermochemical Properties for the Various Species at Room Temperature (T = 298.15 K)[a]

complex	entropy (S), J/(mol·K)	thermal function $H(T)$, kJ/mol	C_p, J/(mol·K)
UF_6	377 (387)	59 (57)	127 (131)
cis-$UO_2(OH)_2$	349 (357)	109 (107)	102.5 (101)
trans-$UO_2(OH)_2$	349 (357)	109 (107)	102.3 (101)
UO_3	301 (304)	36 (34)	61 (63)
HF	191 (191)	35 (29)	29 (32)
H_2O	187 (187)	68 (62)	33 (34)
UO_2F_2	334 (339)	44 (42)	82 (85)

[a] Values in parentheses are obtained with frequencies scaled by 0.9.

and the vibrational frequencies are given in Table 8 as compared with our results. UO_3 has been studied previously at the SCF level by Pyykkö et al.[26] and by Zhou et al.[27] using B3LYP. However, the perfect T-shaped structure of uranium trioxide was not reproduced; the experimental geometry may be a result of the argon matrix. We find, in agreement with the previous studies, a planar C_{2v} structure with two short and one longer U−O bond, where the former correspond to the normal uranyl bonds. Our result for the two short bonds is 0.08 Å shorter than the B3LYP result of Zhou et al., which is the typical SCF error (see discussion above). The longer bond as obtained by us is 0.02 Å shorter than the B3LYP result, a deviation that may be caused either by the lack of correlation in the SCF calculations or by the larger core used by Zhou et al.

The vibration frequencies are in reasonable agreement with theoretical and experimental results available in the literature, with three low bending modes and three higher stretching modes. Zhou et al. only give stretching vibrational frequencies. Our stretching frequencies are about 10% higher than those reported by Zhou et al., as may be expected because frequencies have been calculated at the SCF level.[28]

3.2. Energetics and Reaction Enthalpies. The calculated reaction enthalpy $\Delta_f H^\circ_m$ 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 the ZPE (zero-point vibration energy) correction.[28] 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 28). The theoretical values for $H(T)$ are obtained from calculated geometries and vibration spectra. The entropy, the heat capacity, and the thermal function $H(T)$ are shown in Table 9, whereas Table S2 (Supporting Information) shows the total energy in atomic units for all species involved in the reactions 1−5.

Vibration frequencies calculated at the SCF level are normally overestimated by about 10%. A common procedure is therefore to scale down the calculated frequencies with the factor 0.9 (see ref 28). We have included thermodynamic quantities obtained using the scaled vibration frequencies within parentheses in Table 9. The effect of scaling is minor because the vibration contribution to the thermodynamic quantities is small (see above and Table S1).

Table 10 shows the reaction enthalpies obtained at the SCF and correlated levels for reactions 1−5 and the corresponding experimental values. For completeness we also show the changes in $H(T = 298.15\ K)$ for the reactions in Table S3.

The data labeled experimental in our study are taken from refs 3 and 4 and are derived from a combination of experiments and theory. The uncertainties in the reported energies of formation varies from 2 kJ/mol for UF_6(g) to 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).

The agreement between the experimental and the calculated reaction enthalpies for reactions 1 and 4 in our most accurate calculations (CCSD(T)) is actually better than expected from the uncertainties in the experimental values, whereas the results are surprisingly poor for reactions 2, 3, and 5. The same trend, but much less pronounced, can be seen for the less accurate MP2 results and the B3LYP results.

One evident source of errors in the present calculations is the difficulty in describing the fluoride ion. The size of the complexes studied does not allow us to use extended basis sets, and it is well-known that the fluoride ion is poorly described in limited basis set CI calculations due to the diffuse character of the ion and the importance of low excitations such as 2p → 3p. A common feature of reactions 2, 3, and 5 is that HF appears among the reaction products and moreover an increasing error at the CCSD(T) level from 46 kJ/mol for reaction 2 with two HF to 76 kJ/mol for reaction 3 with four HF and to 123 kJ/mol for reaction 5 with six HF. On the other hand the errors for reactions 1 and 4, where HF is not a reaction product, are only 18 and 2 kJ/mol, respectively. This result indicates that the error in the description of the fluoride ion cancels for the complexes but not for HF.

Assuming this to be the case, it is possible to estimate a correction by comparing experimental and theoretical data for some selected reaction, either one of 2, 3, or 5, or some other reaction.

The simplest possible reaction that can be used is

$$H_2 + F_2 \rightarrow 2HF \tag{9}$$

The advantage of using this reaction to calibrate the other results is that it is simple and experimentally well-known, the disadvantage is that it is far from evident that the errors associated

TABLE 10: Calculated and Experimental Reaction Enthalpy for Reactions 1−5

reaction	SCF	MP2	CCSD(T)	B3LYP	exp
$2UO_3 + UF_6 \rightarrow 3UO_2F_2$	−567 (−257)	−278 (32)	−329 (−18)	−262 (49)	−311
$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	131.20 (66.70)	101 (36)	110 (46)	130 (65)	65
$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$	170 (−17)	232 (45)	263 (76)	332 (145)	187
$UO_3 + H_2O \rightarrow UO_2(OH)_2$	−237 (−53)	−154 (30)	−186 (−2)	−166 (18)	−184
$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$	539 (104)	487 (51)	558 (123)	627 (192)	435

[a] The difference between theory based and experimental data are given in parentheses. The energy is in kJ/mol.

TABLE 11: Corrected Reaction Enthalpies (kJ/mol) Using the $H_2 + F_2 \rightarrow 2HF$ Reaction[a]

reaction	MP2	CCSD(T)	B3LYP	exp
$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	117 (52)	79 (14)	88 (23)	65
$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$	263 (76)	200 (13)	246 (59)	187
$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$	534 (99)	464 (29)	500 (65)	435

[a] Deviations from experiment within parentheses.

TABLE 12: Corrected Reaction Enthalpies, in kJ/mol, Using Reaction 3[a]

reaction	MP2	CCSD(T)	B3LYP	exp
$2UO_3 + UF_6 \rightarrow 3UO_2F_2$	−278 (32)	−329 (−18)	−262 (49)	−311
$UO_2F_2 + 2H_2O \rightarrow UO_2(OH)_2 + 2HF$	79 (14)	72 (7)	58 (6)	64
$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$	187 (0)	187 (0)	187 (0)	187
$UO_3 + H_2O \rightarrow UO_2(OH)_2$	−154 (30)	−186 (−2)	−166 (18)	−184
$UF_6 + 3H_2O \rightarrow UO_3 + 6HF$	419 (−16)	444 (9)	411 (−24)	435

[a] Deviations from experiment within parentheses. Corrections applied for reactions 2, 3, and 5. Reactions 1 and 4 are not affected by the correction but are included in the table for completeness.

with the F_2 molecule will cancel those associated with the fluoride ion in the uranium compounds.

The reaction enthalpies for reaction 9 at 298.15 K are −563, −516, and −504 kJ/mol at the MP2, CCSD(T), and B3LYP levels, respectively. The reaction enthalpy at the SCF level is −581 kJ/mol, and the effect of correlation is thus in all cases to decrease the energy needed to form HF. However, CCSD(T) and B3LYP underestimate this energy and MP2 overestimates it. The most likely reason for this discrepancy is the description of the F_2 molecule; MP2 is known to perform badly for light homonuclear diatomic molecules, resulting in an overestimated correlation energy for F_2.

Using these results, we can determine a correction for the reactions involving HF. We have assumed, as described above, that the error for reactions 2 and 3 and 9 is mainly related to the description of HF, and that the errors associated with fluoride ions in the uranium complexes and in F_2 cancel. The correction factor for reactions 2, 3, and 5 is then the difference between the experimental and theoretical result in Table 11. For example, CCSD(T) underestimates the reaction enthalpy by 31.3 kJ/mol. Using this correction, the reaction enthalpy for reaction 2 becomes 110 − 31 = 79 kJ/mol and for reaction 3 263 − 63 = 200 kJ/mol, in much better agreement with the experimental data, 65 and 187 kJ/mol, respectively. In Table 11 we give the corrected reaction enthalpies for reactions 2, 3, and 5.

The correction improves the results obtained at the CCSD(T) and B3LYP levels dramatically, in particular for reaction 5, whereas the MP2 results actually get worse. As discussed above, this is most likely due to a poor description of F_2 at the MP2 level; as a result, the errors no longer cancel between F_2 and the complexes. Clearly, reaction 9 cannot be used as a reference reaction at the MP2 level, and it is in fact surprising that the correction works as well as it does at the CCSD(T) level given the difference in binding in F_2 and the fluoride ion in the uranium compounds.

An alternative, which avoids this problem, is to use one of the reactions 2, 3, or 5 as the reference reaction. The result of using reaction 3 as the basis for the correction instead of the reaction 9 is shown in Table 12. For completeness we have also included the reaction enthalpies for reactions 1 and 4 from Table 10, although these reactions are not affected by the correction. The results improve at all levels, but at the MP2 level the improvement is dramatic. The MP2 error decreases from 52 to 14 kJ/mol for reaction 2 and from 99 to 16 kJ/mol for reaction 5.

This shows that it is possible to make reliable estimates of reaction enthalpies for a series of reactions by calibrating to some appropriate experimental reaction enthalpy. The results also provide strong evidence that the problem is indeed associated with HF. For completeness one should also point out that a similar approach might be applied for the calculations of the Gibbs energy of reaction.

4. Conclusion

In the present article, we have shown that it is possible to estimate reliable reaction data for uranium(VI) complexes in the gas phase by using a known model reaction for calibration. Thermodynamic quantities such as the entropy and the enthalpy can be calculated with sufficient accuracy from theoretical geometries and vibration frequencies. We have shown that there are cases where the thermal functions are fairly insensitive to the vibration frequencies, despite large errors in the assumed geometry and vibration frequencies.

The methodology presented here can in principle be used to determine reaction data for less known gas phase systems, such as neptunium or plutonium complexes. A complication for the heavier actinides is the presence of open f-shells, which precludes the use of CCSD(T) for actinides heavier than neptunium. However, we have shown that an acceptable accuracy can be obtained already at the MP2 and DFT levels if the calibration reaction is properly chosen. According to our experience from the previous study of the reduction of MO_2^{2+}, where M is U, Np, Pu, or Am, it may be possible to use a correction determined for uranium also for heavier actinides. Studies along these lines have been initiated in our laboratory. In the case of trans-uranium actinides spin−orbit effects have to be accounted for. Previous experience, for example, the electronic spectrum of NbO and PuO_2^{2+}, shows that also these effects can be treated quite accurately at a small computational cost (see refs 28 and 29). The present results can also be used as a starting point for the more difficult case to calculate reaction data in solution.

The entropy and the heat capacity for UO_2F_2 have previously been estimated using rather crude estimates of both the vibration spectrum and the geometry. Surprisingly, the difference between the estimated and properly calculated entropies and heat capacities for this compound are quite similar. The calculated vibration spectrum of UF_6 is in good agreement with experiment for the lower part of the spectrum.

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Supporting Information Available: Tables of entropy and heat capacity contributions, total energies, and enthalpies. This material is available free of charge via the Internet at http://pubs.acs.org.

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