

# The Heat of Formation of the Uranyl Dication: Theoretical Evaluation Based on Relativistic Density Functional Calculations

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**Abstract:** By using a set of model reactions, we estimated the heat of formation of gaseous  $\text{UO}_2^{2+}$  from quantum-chemical reaction enthalpies and experimental heats of formation of reference species. For this purpose, we performed relativistic density functional calculations for the molecules  $\text{UO}_2^{2+}$ ,  $\text{UO}_2$ ,  $\text{UF}_6$ , and  $\text{UF}_5$ . We used two gradient-corrected exchange-correlation functionals (revised Perdew–Burke–Ernzerhof (PBEN) and Becke–Perdew (BP)) and we accounted for spin-orbit inter-

action in a self-consistent fashion. Indeed, spin-orbit interaction notably affects the energies of the model reactions, especially if compounds of  $\text{U}^{\text{IV}}$  are involved. Our resulting theoretical estimates for  $\Delta_f H_0^\circ(\text{UO}_2^{2+})$ ,  $365 \pm 10 \text{ kcal mol}^{-1}$  (PBEN) and  $370 \pm 12 \text{ kcal mol}^{-1}$  (BP), are in quantitative

agreement with a recent experimental result,  $364 \pm 15 \text{ kcal mol}^{-1}$ . Agreement between the results of the two different exchange-correlation functionals PBEN and BP supports the reliability of our approach. The procedure applied offers a general means to derive unknown enthalpies of formation of actinide species based on the available well-established data for other compounds of the element in question.

**Keywords:** actinides • density functional calculations • heats of formation • relativistic effects • uranyl

## Introduction

Recent computational studies of actinide compounds have provided valuable information to complement the knowledge accumulated from experimental work. Aside from precise structural characteristics of large polyatomic molecules,<sup>[1]</sup> thermophysical properties, such as reaction energies,<sup>[2,3]</sup> solvation energetics,<sup>[4–6]</sup> or ionization potentials,<sup>[7]</sup> can be predicted with reasonable accuracy. Computational methods are especially useful for species that are difficult to isolate experimentally, such as ions in the gas phase. For instance, theoretical results<sup>[7,8]</sup> prompted a recent reevaluation of the first ionization potential of the molecule  $\text{UO}_2$ , whereby more sophisticated spectroscopic techniques<sup>[9]</sup> produced a result  $\sim 0.6 \text{ eV}$  higher than that accepted previously. This new value requires a reconsideration of the accepted heat of formation of  $\text{UO}_2^+$ , and eventually of other thermochemical data that depend on the above property.

Reliable experimental thermochemistry data for actinide compounds are quite scarce. Although the uranyl dication  $\text{UO}_2^{2+}$  is among the most-studied actinide species, the precise heat of formation in the gas phase, even for this molecule, is not known. Marcus<sup>[10,11]</sup> first recommended the value  $\Delta_f H_{298}^\circ(\text{UO}_2^{2+}(\text{g})) = 289.2 \pm 4.8 \text{ kcal mol}^{-1}$ , calculated from a complex thermodynamic cycle.<sup>[11]</sup> Two measurements employing Fourier transform ion-cyclotron resonance (FTICR) mass spectrometry<sup>[12,13]</sup> provided lower and upper limits,  $311 \text{ kcal mol}^{-1} \leq \Delta_f H^\circ \leq 430 \text{ kcal mol}^{-1}$ <sup>[12]</sup> and, very recently, a revised interval of  $284 \text{ kcal mol}^{-1} \leq \Delta_f H^\circ \leq 405 \text{ kcal mol}^{-1}$ .<sup>[13]</sup> For both sets of results, the upper limit was derived from a lower limit for the bond-dissociation energy of  $\text{UO}_2^+ - \text{O}$  and the heat of formation of  $\text{UO}^+$ ; the lower limit was based on the occurrence of electron transfer from  $\text{N}_2\text{O}$  to  $\text{UO}_2^{2+}$ . Although the two values for the lower limit are close to the value recommended by Marcus, the mid-points of both intervals lie well above this value.<sup>[11]</sup> For the recent interval, Gibson et al.<sup>[13]</sup> used revised values for the heats of formation of  $\text{UO}_2^+$  and  $\text{UO}^+$ . They also proposed a more accurate estimate of  $\Delta_f H^\circ(\text{UO}_2^{2+}(\text{g})) = 364 \pm 15 \text{ kcal mol}^{-1}$  on the basis of their measured ionization energy  $\text{IE}(\text{UO}_2^+) = 14.6 \pm 0.4 \text{ eV}$ <sup>[13]</sup> and the literature values  $\text{IE}(\text{UO}_2(\text{g})) = 6.128 \text{ eV}$ <sup>[9]</sup> and  $\Delta_f H^\circ(\text{UO}_2(\text{g})) = 111 \pm 1 \text{ kcal mol}^{-1}$ .<sup>[14]</sup>

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Precise knowledge of the formation enthalpy of “bare”  $\text{UO}_2^{2+}(\text{g})$  is essential for deriving the “experimental” enthalpy of hydration as  $\Delta_{\text{h}}H^\circ(\text{UO}_2^{2+}) = \Delta_{\text{f}}H^\circ(\text{UO}_2^{2+}(\text{aq,abs})) - \Delta_{\text{f}}H^\circ(\text{UO}_2^{2+}(\text{g}))$  and the related Gibbs free energy of hydration,  $\Delta_{\text{h}}G^\circ(\text{UO}_2^{2+}) = \Delta_{\text{h}}H^\circ(\text{UO}_2^{2+}) - T\Delta_{\text{h}}S^\circ(\text{UO}_2^{2+})$ . The value of  $\Delta_{\text{f}}H^\circ(\text{UO}_2^{2+}) = 325.3 \pm 5.5 \text{ kcal mol}^{-1}$  that is given in the Gmelin Handbook<sup>[15]</sup> is based on the old recommendation by Marcus,<sup>[10,11]</sup> in view of the recent measurements,<sup>[12,13]</sup> this value must be reconsidered. Recently, we reported a theoretical study of the hydration free energy of the uranyl dication.<sup>[5]</sup> Our result,  $\Delta_{\text{h}}G^\circ(\text{UO}_2^{2+}) = -370 \text{ kcal mol}^{-1}$ , was consistent with the “experimental” estimates that were derived from more recent determinations of  $\Delta_{\text{f}}H^\circ(\text{UO}_2^{2+})$ .<sup>[12,13]</sup> However, even the most recent measurement of the heat of formation of uranyl contains an uncertainty of  $30 \text{ kcal mol}^{-1}$ .<sup>[13]</sup>

This margin can be further reduced by employing a theoretical value of  $\Delta_{\text{f}}H^\circ(\text{UO}_2^{2+})$ , based on well-known heats of formation of other uranium compounds. Here, we address this issue by exploiting the predictive power of contemporary quantum-chemistry methods.

## Computational Methods

We performed all-electron calculations by using the linear combination of Gaussian-type orbitals fitting-functions density functional method<sup>[16]</sup> (LCGTO-FF-DF), as implemented in the code PARAGAUSS.<sup>[17,18]</sup> Relativistic effects were taken into account by invoking a second-order Douglas-Kroll (DK) transformation to decouple electronic and positronic degrees of freedom of the Dirac-Kohn-Sham equation.<sup>[19,20]</sup> We used two variants of this methodology. In the standard scalar-relativistic (SR) variant, only the nuclear part  $v_{\text{nuc}}$  of the effective one-electron potential is used to define the decoupling transformation (DKnuc-SR) and is relativistically transformed. In that variant, the electron-electron contributions  $v_{\text{ee}}$  to the effective potential, both the classical Coulomb (Hartree) part  $v_{\text{Coul}}$  and the exchange-correlation potential  $v_{\text{xc}}$ , remain unchanged, as in the nonrelativistic approach. For molecules containing uranium, the splitting of one-electron levels due to spin-orbit interactions becomes non-negligible. Recently, we introduced an extension of the two-component Douglas-Kroll formalism (DK $n$ ,  $n = 1-3$ ),<sup>[21-23]</sup> which incorporates scalar-relativistic as well as spin-orbit effects, due to a relativistic treatment of both  $v_{\text{nuc}}$  and  $v_{\text{Coul}}$ . Moreover, the relativistic transformation, in general dependent on the effective one-electron potential, is improved by contributions from  $v_{\text{Coul}}$  to first order.<sup>[21]</sup>

We optimized the molecular structures at the DKnuc-SR level, employing the local-density approximation (LDA) in the parameterization of Vosko, Wilk, and Nusair (VWN)<sup>[24]</sup> because LDA often yields more accurate results for molecular geometries.<sup>[25,26]</sup> In the geometry optimizations, the total energy and elements of the density matrix were required to converge to  $10^{-8}$  au; for the largest component of the forces and the geometry update step, the convergence criteria were set to  $10^{-5}$  au.

On the other hand, gradient-corrected functionals (generalized gradient approximation, GGA) are known to perform better for energy parameters.<sup>[25,26]</sup> Therefore, based on the structures obtained at the LDA level, we subsequently refined the energetics in single-point fashion with two GGA functionals; those suggested by (i) Becke and Perdew (BP),<sup>[27,28]</sup> and (ii) Perdew, Burke, and Ernzerhof in the modified form of Nørskov et al. (PBEN).<sup>[29]</sup> As a first step, the specified GGA calculations were performed by using the same DKnuc-SR approach for relativistic transformations. The corresponding reaction enthalpies in Table 1 are denoted with the shortened notation “SR”.

To achieve higher accuracy in energetics, we also performed single-point BP and PBEN calculations at the first-order DKee level, DKee1.<sup>[21]</sup> The difference  $\Delta E$  between the energies from relativistic DKee1 and scalar-relativistic DKnuc-SR calculations (PBEN values are listed in Table 1) shows quantitatively the effect of relativistic terms that are neglected in the DKnuc-SR approximation (mainly spin-orbit interaction).  $\Delta E$  values calculated by using the BP functional (not shown in Table 1) differed from the PBEN values by  $0.25 \text{ kcal mol}^{-1}$  at most. Test calculations have shown that the variant DKee1 is sufficiently accurate for the present purpose. The difference in the reaction energies for the  $\text{UF}_6 = \text{UF}_3 + 1/2\text{F}_2$  reaction at the levels<sup>[21]</sup> DKee1 and DKee2 was less than  $0.2 \text{ kcal mol}^{-1}$ . To determine the correction  $\Delta E$  for open-shell systems, we neglected the spin dependence of the exchange-correlation functional.

The Kohn-Sham orbitals were represented by flexible Gaussian-type basis sets, contracted in a generalized fashion by using atomic eigenvectors of scalar-relativistic LDA calculations. For the geometry optimizations at the LDA level, we used standard basis sets for O, C, N, and F,<sup>[30]</sup> (9s,5p,1d)→[5s,4p,1d] and for H, (6s,1p)→[4s,1p].<sup>[30]</sup> For U, we employed a basis set of the type (24s,19p,16d,11f), contracted to [10s,7p,7d,4f]<sup>[31]</sup>. The subsequent single-point GGA calculations were performed with more flexible basis sets to achieve a higher accuracy of the energetics, particularly in DKee1 calculations: (14s,9p,4d)→[5s,4p,2d] for O, C, N, and F,<sup>[32]</sup> (8s,4p,3d)→[4s,3p,2d] for H,<sup>[32]</sup> and uncontracted basis (35s,26p,18d,13f) for U.<sup>[33]</sup> To increase the accuracy, we additionally used 13 g-type exponents in the relativistic transformations, numerically identical to those of the f set.

The auxiliary basis set utilized in the LCGTO-FF-DF method to represent the electron-charge density for treating the Hartree part of the electron-electron interaction was constructed by properly scaling the s and p exponents of the orbital basis sets by using a standard procedure;<sup>[16]</sup> “polarization exponents” were added as geometric series with factors 2.5, starting with 0.1 for p, 0.2 for d, and 0.3 for f exponents.<sup>[16]</sup> The resulting auxiliary basis sets were of the type (8s,4r<sup>2</sup>,5p,5d) for H, (14s,9r<sup>2</sup>,5p,5d) for C, N, O, F, and (35s,13r<sup>2</sup>,5p,5d,5f) for U. The grid for the numeric integration of the exchange-correlation functional consisted of about 26000 points for U, 11400 points for C, 10700 points for N, 9900 points for O, 8500 points for F, and 8900 points for H centers.

## Results and Discussion

To calculate the heat of formation  $\Delta_{\text{f}}H_0^\circ$  of a molecule ( $\text{UO}_2^{2+}$  in the present case) in the gas phase, a model reaction (not necessarily chemically meaningful) is used, in which the enthalpies of formation of all reactants and products, except of the one of interest, are known. Suitable example reactions R1–R21, in which  $\text{UO}_2^{2+}$  appears as one of the products, are listed in Table 1. The enthalpy  $\Delta_{\text{R}i}H_0^\circ$  of reaction  $R_i$  ( $i = 1-21$ ) at 0 K is represented by Equation (1):

$$\Delta_{\text{f}}H_0^\circ(\text{UO}_2^{2+}) = \Delta_{\text{R}i}H_0^\circ + \sum_{\text{reactants}} \Delta_{\text{f}}H_0^\circ - \sum_{\text{products} \neq \text{UO}_2^{2+}} \Delta_{\text{f}}H_0^\circ \quad (1)$$

Our strategy for evaluating  $\Delta_{\text{f}}H_0^\circ(\text{UO}_2^{2+}(\text{g}))$  is based on the selection of model reactions  $R_i$  for which the  $\Delta_{\text{f}}H_0^\circ$  values for all other reactant and product species are known, and in which  $\Delta_{\text{R}i}H_0^\circ$  is evaluated by using a suitable quantum-chemistry method.

In the following, we take 0 K as the reference temperature because at this hypothetical temperature the relationship between quantum-chemical reaction energies and enthalpies is most direct. Thus, we can calculate the heat of

Table 1. Enthalpy of formation  $\Delta_f H_0^\circ$  of  $\text{UO}_2^{2+}(\text{g})$  [ $\text{kcal mol}^{-1}$ ]<sup>[a]</sup> from various formal reactions  $R_i$  ( $i=1-21$ ) based on reaction enthalpies  $\Delta_{R_i} H_0^\circ$  calculated by using the BP or PBEN exchange-correlation functionals at the scalar-relativistic DKnuc level (SR) and at the DKee1 level including spin-orbit interaction, and on experimental thermochemical data.<sup>[b]</sup>

		$\Delta_{R_i} H_0^\circ$ (SR) <sup>[c]</sup>		$\Delta_f H_0^\circ$ (SR)		$\Delta_f H_0^\circ$ (DKee1) <sup>[d]</sup>	
		BP	PBEN	BP	PBEN	$\Delta E$ <sup>[e]</sup>	PBEN
R1	$\text{UF}_6 + 2\text{HCO}^+ + 3\text{H}_2 = \text{UO}_2^{2+} + 2\text{CH}_4 + 3\text{F}_2$	463	452	377	365	4.5	370
R2	$\text{UF}_6 + 2\text{CO}^+ + 4\text{H}_2 = \text{UO}_2^{2+} + 2\text{CH}_4 + 3\text{F}_2$	266	259	376	370	5.2	375
R3	$\text{UF}_6 + 2\text{NO}^+ + 3\text{H}_2 = \text{UO}_2^{2+} + \text{N}_2 + 6\text{HF}$	39	32	384	377	4.4	381
R4	$\text{UF}_6 + 2\text{NO}^+ = \text{UO}_2^{2+} + \text{N}_2 + 3\text{F}_2$	415	404	371	361	4.5	366
R5	$\text{UF}_6 + 2\text{NO}^+ = \text{UO}_2^{2+} + 2\text{NF}_3$	338	337	355	354	4.5	358
R6	$\text{UF}_6 + 2\text{CN}^+ + 2\text{H}_2\text{O} + 2\text{H}_2 = \text{UO}_2^{2+} + 2\text{HCN} + 6\text{HF}$	-174	-182	377	370	4.5	375
R7	$\text{UF}_6 + 2\text{CN}^+ + 2\text{H}_2\text{O} = \text{UO}_2^{2+} + 2\text{HCN} + 3\text{F}_2 + \text{H}_2$	201	191	365	354	4.6	359
R8	$\text{UF}_6 + 2\text{CN}^+ + 2\text{H}_2\text{O} + 2\text{H}_2 = \text{UO}_2^{2+} + 2\text{NF}_3 + 2\text{CH}_4$	29	30	350	350	4.5	354
Average <sup>[f]</sup> R1–R8				369 ± 12	363 ± 10		367 ± 10
R9	$\text{UF}_5 + 2\text{HCO}^+ + 3\text{H}_2 = \text{UO}_2^{2+} + 2\text{CH}_4 + \frac{5}{2}\text{F}_2$	399	391	366	358	5.2	363
R10	$\text{UF}_5 + 2\text{CO}^+ + 4\text{H}_2 = \text{UO}_2^{2+} + 2\text{CH}_4 + \frac{5}{2}\text{F}_2$	201	198	365	362	6.0	368
R11	$\text{UF}_5 + 2\text{NO}^+ + \frac{5}{2}\text{H}_2 = \text{UO}_2^{2+} + \text{N}_2 + 5\text{HF}$	37	33	371	367	5.2	373
R12	$\text{UF}_5 + 2\text{NO}^+ = \text{UO}_2^{2+} + \text{N}_2 + \frac{5}{2}\text{F}_2$	350	344	361	354	5.2	359
R13	$\text{UF}_5 + 2\text{NO}^+ + \frac{1}{2}\text{F}_2 = \text{UO}_2^{2+} + 2\text{NF}_3$	274	276	344	346	5.2	351
R14	$\text{UF}_5 + 2\text{CN}^+ + 2\text{H}_2\text{O} + \frac{3}{2}\text{H}_2 = \text{UO}_2^{2+} + 2\text{HCN} + 5\text{HF}$	-176	-180	365	360	5.2	365
R15	$\text{UF}_5 + 2\text{CN}^+ + 2\text{H}_2\text{O} = \text{UO}_2^{2+} + 2\text{HCN} + \text{H}_2 + \frac{5}{2}\text{F}_2$	137	130	354	347	5.3	352
R16	$\text{UF}_5 + 2\text{CN}^+ + 2\text{H}_2\text{O} + \frac{1}{2}\text{F}_2 + 2\text{H}_2 = \text{UO}_2^{2+} + 2\text{NF}_3 + 2\text{CH}_4$	-35	-31	339	343	5.2	348
Average <sup>[f]</sup> R9–R16				358 ± 11	355 ± 9		360 ± 9
R17	$\text{UO}_2 + 2\text{CO}^+ = \text{UO}_2^{2+} + 2\text{CO}$	-163	-165	373	371	11.3	382
R18	$\text{UO}_2 + 2\text{CO}^+ + \text{H}_2 = \text{UO}_2^{2+} + 2\text{HCO}$	-107	-107	353	353	12.0	365
R19	$\text{UO}_2 + 2\text{HCO}^+ = \text{UO}_2^{2+} + 2\text{HCO}$	90	85	354	349	11.3	361
R20	$\text{UO}_2 + 2\text{NO}^+ = \text{UO}_2^{2+} + 2\text{NO}$	47	44	363	361	10.9	372
R21	$\text{UO}_2 + 2\text{CN}^+ = \text{UO}_2^{2+} + 2\text{CN}$	-189	-190	350	348	11.3	359
Average <sup>[f]</sup> R17–R21				359 ± 9	356 ± 9		368 ± 9

[a] Experimental results:  $311 \text{ kcal mol}^{-1} \leq \Delta_f H^\circ \leq 430 \text{ kcal mol}^{-1}$ ,<sup>[12]</sup>  $364 \pm 15 \text{ kcal mol}^{-1}$ .<sup>[13]</sup> [b] See Table 2. [c] Reaction enthalpies  $\Delta_{R_i} H_0^\circ$  approximated as reaction energies from BP or PBEN calculations, corrected for  $\Delta ZPE$  based on the vibrational frequencies in Table 2. [d]  $\Delta_f H_0^\circ$  (SR) corrected by  $\Delta E$ . [e] Correction  $\Delta E$  of the reaction energy (determined at the scalar-relativistic DKnuc level) to account for scalar-relativistic and spin-orbit effects at the DKee1 level; see also reference [21]. [f] The uncertainty intervals are estimated as standard deviations.

formation  $\Delta_f H_0^\circ$  of uranyl at 0 K. Corrections to any desired temperature can be made subsequently by using the heat capacity calculated from the molecular-partition function. The correction from 0 to 298 K is about 1–2  $\text{kcal mol}^{-1}$ , as for most species listed in Table 2.

For the evaluation of heats of formation from heats of reaction, it is recommended<sup>[34]</sup> to use well-balanced reactions (isodesmic or at least isogyric) whenever possible to benefit from the cancellation of inherent computational errors. The identification of such favorable reactions is not a simple task for the present case, because accurate thermodynamic data for uranium compounds in the gas phase are limited and because ions are involved, which may lead to large reaction ener-

Table 2. Experimental enthalpies of formation [ $\text{kcal mol}^{-1}$ ] and vibrational frequencies [ $\text{cm}^{-1}$ ] of selected molecules and ions in the gas phase<sup>[a]</sup>.

	$\Delta_f H_0^\circ$	$\Delta_f H_{298}^\circ$	Vibrational frequencies
$\text{UF}_6$	-512.1 <sup>[b]</sup>	-513.4 ± 0.4 <sup>[c]</sup>	140 × 3, 184 × 3, 201 × 3, 535 × 2, 624 × 3, 667 <sup>[d]</sup>
$\text{UF}_5$	-459.9 <sup>[b,e]</sup>	-461.0 ± 2.4 <sup>[c]</sup>	648, 572, 129, 515, 99, 201, 593 × 2, 201 × 2, 182 × 2 <sup>[f]</sup>
$\text{UO}_2$	-110.6 <sup>[b,e]</sup>	-111 ± 1 <sup>[g]</sup>	880, 222 × 2, 933 <sup>[h]</sup>
$\text{H}_2\text{O}$	-57.11 <sup>[i]</sup>	-57.80 ± 0.01 <sup>[i]</sup>	3657, 1595, 3756 <sup>[j]</sup>
$\text{H}_2$	0	0	4401.2 <sup>[i]</sup>
$\text{F}_2$	0	0	916.6 <sup>[i]</sup>
HF	-64.69 <sup>[i]</sup>	-64.7 ± 0.3 <sup>[i]</sup>	4138.3 <sup>[i]</sup>
$\text{HCO}^+$	197.3 <sup>[k]</sup>	197.6 ± 2 <sup>[k]</sup>	3088.7, 829.7 × 2, 2183.9 <sup>[l]</sup>
HCO	10.0 <sup>[i]</sup>	10.0 ± 1.0 <sup>[i]</sup>	2434.5, 1868.2, 1080.8 <sup>[l]</sup>
$\text{CO}^+$	295.96 ± 0.13 <sup>[i]</sup>	298.23 <sup>[i]</sup>	2215 <sup>[m]</sup>
CO	-27.20 <sup>[k]</sup>	-26.42 ± 0.04 <sup>[k]</sup>	2169.8 <sup>[i]</sup>
$\text{CH}_4$	-15.92 <sup>[i]</sup>	-17.82 ± 0.07 <sup>[i]</sup>	2917, 1534 × 2, 3019 × 3, 1306 × 3 <sup>[i]</sup>
NO	21.46 <sup>[k]</sup>	21.58 ± 0.04 <sup>[k]</sup>	1904 <sup>[i]</sup>
$\text{NO}^+$	235.2 <sup>[k]</sup>	236.7 ± 0.2 <sup>[k]</sup>	2376.7 <sup>[n]</sup>
CN	104.4 <sup>[i]</sup>	105.2 ± 1.2 <sup>[i]</sup>	2069 <sup>[i]</sup>
$\text{CN}^+$	428.6 <sup>[k]</sup>	430.9 ± 3 <sup>[k]</sup>	2000.8 <sup>[n]</sup>
$\text{NF}_3$	-30.20 <sup>[k]</sup>	-31.57 ± 0.27 <sup>[k]</sup>	1032, 647, 907 × 2, 492 × 2 <sup>[i]</sup>
$\text{UO}_2^{2+}$	365 ± 10 <sup>[o]</sup>		999, 208 × 2, 1102 <sup>[p]</sup>

[a] These species were used to determine the heat of formation of  $\text{UO}_2^{2+}(\text{g})$  based on the formal reactions listed in Table 1. Vibrational frequencies were taken from experimental data where available, otherwise theoretical results were employed. [b] Reference [42]. [c] Reference [44]. [d] Reference [37]. [e] Reference [45]. [f] Reference [38]; only  $\nu_1$ ,  $\nu_2$ , and  $\nu_7$  were measured directly. [g] Reference [14]. [h] Calculated (B3LYP).<sup>[36]</sup> [i] Reference [46]. [j] Reference [47]. [k] Reference [43]. [l] Reference [48]. [m] Reference [49]. [n] Reference [50]. [o] This work. [p] Calculated (PBEN).<sup>[41]</sup>

gies. Although reactions R1, R3–R8, and R18–R21 are isogyric (the number of electron pairs remains constant during the course of the reaction), only the reactions R1, R5, R6, R19, R20, and R21 are formally isodesmic (isogyric reactions in which the numbers of bonds of each formal type are the same for reactants and products). Nevertheless, given their rather large reaction enthalpies, we do not regard these reactions to be particularly well balanced compared to others. Ultimately, we will compare results from isodesmic reactions alone with those derived from the extended set.

The selected formal reactions (Table 1) involve uranium species  $\text{UF}_6$ ,  $\text{UF}_5$ ,  $\text{UO}_2$ , and  $\text{UO}_2^{2+}$  and feature different degrees of balance. Although all four uranium compounds have been studied previously, both theoretically and experimentally,<sup>[7,35–41]</sup> reliable experimental geometries and vibrational frequencies are not available for all of them. Therefore, as a first step, we optimized their geometries (Table 3).

Table 3. Calculated bond lengths [Å] of  $\text{UF}_6$ ,  $\text{UF}_5$ ,  $\text{UO}_2$ , and  $\text{UO}_2^{2+}$  and comparison with experimental data.

Species	Method	Symmetry	State	(U–F), ax	(U–F), eq	(U–O)
$\text{UF}_6$	VWN <sup>[a,b]</sup>	$O_h$	$^1\text{A}_{1g}$	1.998	1.998	–
	B3LYP <sup>[c]</sup>	$O_h$	$^1\text{A}_{1g}$	2.006	2.006	–
	exptl <sup>[d]</sup>	$O_h$	$^1\text{A}_{1g}$	1.999	1.999	–
$\text{UF}_5$	VWN <sup>[a,b]</sup>	$C_{4v}$	$^2\text{B}_2$	2.006	2.010	–
	B3LYP <sup>[c]</sup>	$C_{4v}$	$^2\text{B}_2$	2.030	2.032	–
	exptl <sup>[e]</sup>			2.00	2.02	–
$\text{UO}_2^{2+}$	VWN <sup>[a,b]</sup>	$D_{\infty h}$	$^1\Delta_g^+$	–	–	1.705
	CCSD(T) <sup>[a,f]</sup>	$D_{\infty h}$	$^1\Delta_g^+$	–	–	1.706
	CASPT2 <sup>[a,g]</sup>	$D_{\infty h}$	$^1\Delta_g^+$	–	–	1.705
$\text{UO}_2$	VWN <sup>[a,b]</sup>	$D_{\infty h}$	$^3\Phi_u$	–	–	1.788
	CASPT2 <sup>[a,h]</sup>	$D_{\infty h}$	$^3\Phi_u$	–	–	1.766

[a] All-electron calculation. [b] This work. [c] Reference [35]. [d] Reference [37]. [e] Reference [38]. [f] Reference [39]. [g] Reference [40]. [h] Reference [7].

Our results for the structures and the assigned electronic ground states agree very well with those of other high-level calculations and with the available experimental data. The structures calculated for the other reference species are provided in the Supporting Information.

The enthalpies of formation of all other pertinent species occurring in the reactions R1–R21 have been established previously.<sup>[42–46]</sup> These values are listed in Table 2, together with the vibrational frequencies of all species. We derived reaction enthalpies  $\Delta_{\text{Ri}}H_0^\circ$  from the calculated reaction energies  $\Delta_{\text{Ri}}E$  (see Computational Methods section) by applying a correction for the change  $\Delta\text{ZPE}$  of the zero-point vibrational energies. Where available, we derived the ZPE values from experimental vibrational frequencies,<sup>[36,38,47–50]</sup> exceptions were the compounds  $\text{UO}_2^{2+}$  and  $\text{UO}_2$ , for which we used calculated vibrational frequencies (Table 2). In Table 1, we present the reaction enthalpies  $\Delta_{\text{Ri}}H$  obtained from BP and PBEN calculations, and predictions for the enthalpies of formation  $\Delta_{\text{f}}H_0^\circ(\text{UO}_2^{2+})$  for the reactions R1–R21, resulting from these reaction enthalpies and the data collected in Table 2.

In Table 1, we partitioned the model reactions into three groups involving  $\text{UF}_6$ ,  $\text{UF}_5$ , and  $\text{UO}_2$ . Because the experimental heats of formation of all other model species are known with very high accuracy (Table 2), the main uncertainty in the experimental data arises from the heats of formation of these three uranium compounds.  $\text{UF}_6$  is a stable molecule with a heat of formation,  $\Delta_{\text{f}}H_{298}^\circ(\text{UF}_6(\text{g})) = 513.4 \pm 0.4 \text{ kcal mol}^{-1}$ , that has not been questioned since its measurement in 1979,<sup>[44]</sup>; therefore, we consider this to be a reliable value. The heat of formation of  $\text{UF}_5$ , connected to the bond-dissociation energy in  $\text{UF}_6$ , has been subject to discussion in the literature.<sup>[51–53]</sup> By the careful redetermination of this bond-dissociation energy<sup>[45]</sup> from reduction of  $\text{UF}_6$  by Ag over a broad temperature range, an internally consistent set of heats of formation of gaseous  $\text{UF}_n$  species became available, which gained high confidence. The resulting recommended value  $\Delta_{\text{f}}H_{298}^\circ(\text{UF}_5) = -461.0 \pm 2.4 \text{ kcal mol}^{-1}$  translates into  $\Delta_{\text{f}}H_0^\circ(\text{UF}_5) = -459.9 \pm 2.4 \text{ kcal mol}^{-1}$ .<sup>[42]</sup> This value was confirmed by a more recent measurement,<sup>[54]</sup>  $\Delta_{\text{f}}H_0^\circ(\text{UF}_5) = -457.4 \pm 3.6 \text{ kcal mol}^{-1}$ , which agrees with the former within the experimental errors. To broaden the data set, we also wanted to include a uranium compound free of fluorine. We chose gaseous  $\text{UO}_2$ , whose experimental enthalpy of formation does not depend directly on those of the uranium fluorides. The presently accepted<sup>[14]</sup> standard heat of formation  $\Delta_{\text{f}}H_{298}^\circ(\text{UO}_2(\text{g})) = -111.0 \pm 1.0 \text{ kcal mol}^{-1}$  originates from an analysis of spectroscopic data for gaseous  $\text{UO}_2$ .<sup>[55]</sup> However, lower ( $-129.6 \pm 0.4$ ,<sup>[56]</sup>  $117 \pm 10$ ) as well as higher ( $-96 \text{ kcal mol}^{-1}$ <sup>[57]</sup>) values of  $\Delta_{\text{f}}H_{298}^\circ(\text{UO}_2(\text{g}))$  have also been reported.

The values of  $\Delta_{\text{f}}H_0^\circ(\text{UO}_2^{2+})$  for the model reactions R1–R21 resulting from scalar-relativistic DKnuc calculations at the PBEN level scatter from 343 to 377  $\text{kcal mol}^{-1}$  (Table 1). BP results for  $\Delta_{\text{Ri}}H$  are systematically higher than PBEN results by up to 11  $\text{kcal mol}^{-1}$ . Within each of the three subgroups of Table 1, the BP results also scatter somewhat more than the PBEN values: 34 vs 27  $\text{kcal mol}^{-1}$  ( $\text{UF}_6$ , R1–R8), 32 vs 24  $\text{kcal mol}^{-1}$  ( $\text{UF}_5$ , R9–R16), and 23 vs 23  $\text{kcal mol}^{-1}$  ( $\text{UO}_2$ , R17–R21). This analysis provides some argument that the PBEN energies may be more reliable. Therefore, we based our final values for the reaction energies  $\Delta_{\text{Ri}}H_0^\circ$ , which we corrected for effects of spin-orbit interaction, on the results obtained by using the PBEN functional. Nevertheless, as shown by the addition of  $\Delta E$  corrections to the BP data, a rather similar final result is obtained (see below).

Intuitively, one expects the best cancellation of errors to be for reactions of the third group involving  $\text{UO}_2$ , R17–R21, due to a small number of species and unchanged atomic frameworks. This expectation is further corroborated by the fact that the differences in  $\Delta_{\text{f}}H_0^\circ(\text{UO}_2^{2+})$  between the two GGA exchange-correlation functionals are indeed smaller, 0–5  $\text{kcal mol}^{-1}$ , for these relatively simple reactions (Table 1) than those for the first and second groups, 7 and 5  $\text{kcal mol}^{-1}$  on average, respectively.

To improve the accuracy of the calculated reaction energies, we recalculated all compounds at the more elaborate

relativistic level DKee1.<sup>[21]</sup> The corresponding energy correction  $\Delta E$  (Table 1) increases the reaction energies  $\Delta_{\text{Ri}}H$  of reactions R1–R21 and consequently the resulting values  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+})$ . This relative stabilization of the reactants is attributed mainly to spin-orbit interaction, due to both the nuclear and the Coulomb parts of the effective electron–electron interaction potential, and is expected to be largest for the  $f^2$  system  $\text{UO}_2$ , intermediate for the  $f^1$  system  $\text{UF}_5$ , and smallest for the  $f^0$  systems  $\text{UF}_6$  and  $\text{UO}_2^{2+}$ . In fact, the DKee1 correction  $\Delta E$  is on average similar for the  $\text{UF}_6$  and  $\text{UF}_5$  groups, but two to three times larger for the  $\text{UO}_2$  group (Table 1).

We improved the scalar-relativistic DKnuc PBEN results by  $\Delta E$  and averaged them separately for each group of model reactions (Table 1). At the DKnuc-SR level, the average of the first group ( $\text{UF}_6$ ) was largest,  $363 \text{ kcal mol}^{-1}$ , and that of the  $\text{UF}_5$  group was smallest,  $355 \text{ kcal mol}^{-1}$ . After application of the correction  $\Delta E$ , the estimates of  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+})$  based on  $\text{UF}_6$ ,  $\text{UF}_5$ , and  $\text{UO}_2$  as reference species averaged to  $367 \pm 10$ ,  $360 \pm 9$ , and  $368 \pm 9 \text{ kcal mol}^{-1}$ , respectively. The corrected enthalpy values within each group scatter over intervals of comparable length, 27, 24, and  $23 \text{ kcal mol}^{-1}$ , for the first, second, and third group, respectively.

Because the average values derived from the three groups agree to within  $8 \text{ kcal mol}^{-1}$ , it is meaningful to combine the results from all three groups to give the final estimate at the PBEN level,  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+}) = 365 \pm 10 \text{ kcal mol}^{-1}$ . The corresponding BP value is only  $5 \text{ kcal mol}^{-1}$  higher,  $370 \pm 12 \text{ kcal mol}^{-1}$ . Both results are in excellent agreement with the most recent experimental value  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+}) = 364 \pm 15 \text{ kcal mol}^{-1}$ ,<sup>[13]</sup> and also fall well within the previously determined experimental interval  $311 \text{ kcal mol}^{-1} \leq \Delta_{\text{f}}H^{\circ} \leq 430 \text{ kcal mol}^{-1}$ <sup>[12]</sup> and the revised interval  $284 \text{ kcal mol}^{-1} \leq \Delta_{\text{f}}H^{\circ} \leq 405 \text{ kcal mol}^{-1}$ .<sup>[13]</sup> Interestingly, by taking only the five isodesmic reactions R1, R5, R19, R20, and R21, a value of  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+}) = 364 \pm 6 \text{ kcal mol}^{-1}$  is obtained, which is very close to that calculated from the extended set of the 21 model reactions. This result lends overall support to our procedure.

Finally, we note that the DKee1-corrected energy for the double ionization of  $\text{UO}_2$  to  $\text{UO}_2^{2+}$ ,  $21.0 \text{ eV}$  at the PBEN level ( $21.4 \text{ eV}$  at the BP level), is slightly larger than the sum of the first and second experimental ionization energies,  $20.7 \pm 0.4 \text{ eV}$ .<sup>[9,13]</sup> From this observation, one might anticipate that the stability of  $\text{UO}_2$  relative to  $\text{UO}_2^{2+}$  is overestimated by  $\sim 7 \text{ kcal mol}^{-1}$ , which would then translate into overestimated values of  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+})$  for the corresponding model reactions. The DKee1 values of  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+})$  from reactions R17–R21 agree, on average, with the results of the other two reaction groups (Table 1). Nevertheless, this uncertainty is still within the range of the overall scatter of our results.

## Conclusion

We have used model reactions to derive a “theoretical” value for the heat of formation of  $\text{UO}_2^{2+}$  in the gas phase, based on well-established experimental heats of formation of  $\text{UF}_6(\text{g})$ ,  $\text{UF}_5(\text{g})$ , and  $\text{UO}_2(\text{g})$ . For this purpose, we determined reaction energies from scalar-relativistic all-electron density functional calculations with two GGA functionals, BP and PBEN. To improve the accuracy of these reaction energies, we also employed a more advanced two-component relativistic formalism (DKee1), which includes spin-orbit interaction self-consistently, for both the nuclear and the classical Coulomb parts of the effective one-electron potential. The correction with respect to the scalar-relativistic energetics ranged from  $4.4$  to  $12.0 \text{ kcal mol}^{-1}$  and, not unexpectedly, was largest for reactions based on  $\text{UO}_2$ , in which uranium is formally tetravalent, carrying two unpaired  $f$  electrons. From 21 model reactions, we estimated  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+})$  at  $365 \pm 10 \text{ kcal mol}^{-1}$  at the PBEN level. The corresponding average at the BP level is only slightly larger,  $370 \pm 12 \text{ kcal mol}^{-1}$ . About the same average mismatch of bond-dissociation energies calculated with different GGA functionals,  $3$ – $5 \text{ kcal mol}^{-1}$ , is commonly found.<sup>[25,26]</sup> The consistency of the PBEN and BP results supports the selected set of reactions as being sufficiently balanced and predictive. Our derived heats of formation support the recent experimental value from ion-cyclotron mass-spectroscopic measurements,  $\Delta_{\text{f}}H^{\circ}(\text{UO}_2^{2+}) = 364 \pm 15 \text{ kcal mol}^{-1}$ .<sup>[13]</sup> Indirectly, we also confirm that the experimental enthalpies of formation of uranium fluorides and oxides are mutually consistent. One expects that the remaining uncertainty can be further reduced with the help of higher-level post-HF methods.

A precise knowledge of the heat of formation of uranyl in the gas phase is central to understanding the thermochemistry of this important uranium species. In particular, the heat of formation serves as a reference for the solvation free energy of this dication, which is another important characteristic.<sup>[5]</sup>

The approach applied here to the uranyl dication is sufficiently general for it to be used routinely in filling gaps in the database of known enthalpies of formation of gas-phase actinide molecules and ions. This can be achieved by choosing appropriate reference species with known properties and model reactions, whose energetics can be calculated with good accuracy by using contemporary quantum-chemistry methods.

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