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The heat of formation of gaseous PuO_2^{2+} from relativistic density functional calculations

Lyudmila V. Moskaleva, Alexei V. Matveev, Joachim Dengler, and Notker Rösch

Department Chemie, Theoretische Chemie,
Technische Universität München, 85747 Garching, Germany

Table S1. Cartesian coordinates (in Å, VWN) of various species used in the model reactions R1–R21

Species	Symmetry	Atom	X	Y	Z
PuF_6	O_h	Pu	0.000000	0.000000	0.000000
		F	1.960042	0.000000	0.000000
		F	0.000000	1.960042	0.000000
		F	0.000000	-1.960042	0.000000
		F	-1.960042	0.000000	0.000000
		F	0.000000	0.000000	1.943737
		F	0.000000	0.000000	-1.943737
PuF_4	C_{3v}	Pu	0.000000	0.000000	-1.133427
		F	0.000000	0.000000	0.857939
		F	1.946621	0.000000	-1.610118
		F	-0.973311	1.685823	-1.610118
		F	-0.973311	-1.685823	-1.610118
PuO_2	$D_{\infty h}$	Pu	0.000000	0.000000	0.000000
		O	0.000000	0.000000	1.760479
		O	0.000000	0.000000	-1.760479
PuO_2^{2+}	$D_{\infty h}$	Pu	0.000000	0.000000	0.000000
		O	0.000000	0.000000	1.663157
		O	0.000000	0.000000	-1.663157
HCO^+	$C_{\infty v}$	C	0.000000	0.000000	0.000000
		H	0.000000	0.000000	1.110392
		O	0.000000	0.000000	-1.109466
HCO	C_s	C	0.001018	0.380865	0.000000
		H	-0.478169	1.416027	0.000000
		O	1.165666	0.203984	0.000000
CO^+	$C_{\infty v}$	C	0.000000	0.000000	0.000000
		O	0.000000	0.000000	1.118211
CO	$C_{\infty v}$	C	0.000000	0.000000	0.000000

		O	0.000000	0.000000	1.132409
NO^+	$C_{\infty v}$	N	0.000000	0.000000	-0.001076
		O	0.000000	0.000000	1.119287
NO	$C_{\infty v}$	N	0.000000	0.000000	0.000000
		O	0.000000	0.000000	1.184222
CN^+	$C_{\infty v}$	C	0.000000	0.000000	-0.021360
		N	0.000000	0.000000	1.144916
CN	$C_{\infty v}$	C	0.000000	0.000000	-0.023617
		N	0.000000	0.000000	1.147173
HCN	$C_{\infty v}$	C	0.000000	0.000000	0.000000
		H	0.000000	0.000000	1.078667
		N	0.000000	0.000000	-1.154638
H_2	$D_{\infty h}$	H	0.000000	0.000000	0.383982
		H	0.000000	0.000000	-0.383982
CH_4	T_d	C	0.000000	0.000000	0.000000
		H	0.635080	0.635080	0.635080
		H	0.635080	-0.635080	-0.635080
		H	-0.635080	0.635080	-0.635080
		H	-0.635080	-0.635080	0.635080
F_2	$D_{\infty h}$	F	0.000000	0.000000	0.700384
		F	0.000000	0.000000	-0.700384
N_2	$D_{\infty h}$	N	0.000000	0.000000	0.550759
		N	0.000000	0.000000	-0.550759
HF	$C_{\infty v}$	F	0.000000	0.000000	-0.204553
		H	0.000000	0.000000	0.728439
NF_3	C_{3v}	N	0.000000	0.000000	-0.031510
		F	1.236691	0.000000	0.579409
		F	-0.618346	1.071006	0.579409
		F	-0.618346	-1.071006	0.579409
H_2O	C_{2v}	O	0.000000	0.000000	-0.057858
		H	0.774468	0.000000	0.528929
		H	-0.774468	0.000000	0.528929

Table S2. Total energies (in au) at the GGA-PBEN level of the various species used in model reactions R1–R21, determined in single-point fashion at the DKnuc-SR and the DKee1 levels of theory. To estimate the effect of spin-orbit interaction (ΔE) for open-shell systems, results of DKnuc-SR calculations are also provided, where the dependence of the exchange-correlation functional on the spin density (SD negl.) has been neglected. Two models for estimating Δ*E* were used. M1: high-spin adiabatic model; M2: closed-shell adiabatic model (see text for details).

Species	DKnuc-SR	DKnuc-SR (SD negl.)	DKee1
PuF_6	-30150.987974	-30150.954059 (M1)	-30241.235195 (M1)
		-30151.006693 (M2)	-30241.289937 (M2)
PuF_4	-29951.073672	-29950.976904 (M1)	-30041.246789 (M1)
		-29951.026148 (M2)	-30041.298283 (M2)
PuO_2	-29701.673716	-29701.554547 (M1)	-29791.800360 (M1)
		-29701.623640 (M2)	-29791.880775 (M2)
PuO_2^{2+}	-29700.832632	-29700.805103 (M1)	-29791.058070 (M1)
		-29700.808301 (M2)	-29791.067033 (M2)
HCO^+		-113.665470	-113.674830
HCO	-113.970980	-113.955290	-113.964650
CO^+	-112.916734	-112.883894	-112.893813
CO		-113.425160	-113.435103
NO^+		-129.675900	-129.687010
NO	-130.016700	-130.005110	-130.016520
CN^+		-92.276499	-92.271940
CN	-92.805570	-92.785790	-92.792790
HCN		-93.513220	-93.520190
H_2		-1.178360	-1.178370
CH_4		-40.552110	-40.554750
F_2		-199.749080	-199.768880
N_2		-109.636151	-109.644890
HF		-100.565980	-100.575910
NF_3		-354.500020	-354.534090
H_2O		-76.515050	-76.521800

Table S3. Spin-contamination in terms of expectation values of $\hat{S}^2$ of the Kohn-Sham determinant for Pu species studied in this work, calculated at the DKnuc-SR GGA-PBEN level of theory.

Species	State	$\langle\hat{S}^2\rangle$
PuF_6	$^3T_{1g}$	2.037
PuF_4	$^5A_1$	6.018
PuO_2	$^5\Sigma_g$	6.035
PuO_2^{2+}	^3H_g	2.018
	$^3\Sigma_g$	2.023