Electronic Supplementary Information

The Redox Mechanism of Np^{VI} with Hydrazine: A DFT Study

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Benchmark of functionals and basis sets

As we known, it is crucial to select the appropriate functional and basis set for theoretical study, especially for the relativistic atom such as Np. Therefore, to test the influence of the different functionals and basis sets on the geometries, we have investigated the reactant $[Np^{VI}O_2(H_2O)_5]^{2+}$ and the product $[Np^{V}O_2(H_2O)_5]^{2+}$ as representatives applying with the generalized gradient approximation (GGA, PBE and BP86), hybrid GGA (B3LYP) and hybrid meta GGA (M06) as well as basis sets such as 6-31g*, 6-311+g* and 6-311++g**. The calculated bond lengths of Np^{VI}-O_{yl}, Np^{VI}-O_{eq}, Np^{V}-O_{yl} and Np^{V}-O_{eq} (O_{yl} and O_{eq} refer to the axial oxygen atom and the equatorial oxygen atom, respectively) at the different level of theory are listed in Table S1 of the ESI†. It can be known from it that the calculated Np^{VI}-O_{yl} bond length of 1.739 Å with the B3LYP functional and 6-31g* basis set is almost same with the experimental value of 1.738 Å [1]. Although the relative error of the calculated Np^{VI}-O_{eq} bond length (1.5%) compared with the experimental value [1] using the B3LYP functional and 6-311++g** basis set is the smallest, and the corresponding value (2.0%) using the B3LYP functional and 6-31g* basis set is also acceptable. Besides, the relative error of the Np^{V}-O_{eq} bond length (0.5%) compared to the experimental value [2] using the B3LYP functional and 6-31g* basis set is also the smallest among all the level of theory. The Np^{V}-O_{yl} bond length of 1.831 Å is extremely close to the experimental value of 1.830 Å [2] using the BP86 functional and 6-311+g* basis set, but the relative error of the Np^{V}-O_{yl} bond length (1.6%) using the B3LYP functional and 6-31g* basis set is also acceptable. In summary, the B3LYP functional and 6-31g* basis set for this work is reasonable and acceptable.

Table S1 Np-O Bond Length of $[Np^{VI}O_2(H_2O)_5]^{2+}$ and $[Np^{V}O_2(H_2O)_5]^{2+}$ with Different Functionals and Basis Sets.

Bond length	Basis set	Method				Expt.
		PBE	BP86	B3LYP	M06	
Np^{VI}-O_{yl}	6-31g*	1.760	1.765	1.739	1.715	1.738[a]
	6-311+g*	1.759	1.763	1.735	1.711	
	6-311++g**	1.757	1.761	1.734	1.710	
Np^{VI}-O_{eq}	6-31g*	2.432	2.435	2.430	2.440	2.479[a]
	6-311+g*	2.421	2.421	2.430	2.426	
	6-311++g**	2.435	2.434	2.442	2.439	
Np^{V}-O_{yl}	6-31g*	1.822	1.825	1.801	1.785	1.830[b]
	6-311+g*	1.826	1.831	1.804	1.787	
	6-311++g**	1.819	1.827	1.800	1.775	
Np^{V}-O_{eq}	6-31g*	2.559	2.546	2.541	2.553	2.520[b]
	6-311+g*	2.539	2.538	2.532	2.533	
	6-311++g**	2.552	2.560	2.549	2.531	

[a]The experimental value is derived from ref. [1].

[b]The experimental value is derived from ref. [2].

Table S2 Electron Density [ρ(r), au], Its Laplacian [$\nabla^2\rho$(r), au], and the Total Energy Density [H(r), au] at the BCP of All Species in the Pathway II

	O_{yl}-H[a]			N-H[a]			Np-O_{yl}		
	ρ(r)	$\nabla^2\rho$(r)	H(r)	ρ(r)	$\nabla^2\rho$(r)	H(r)	ρ(r)	$\nabla^2\rho$(r)	H(r)
int1	0.274[b]	-1.240[b]	-0.373[b]	0.062[b]	0.139[b]	-0.008[b]	-	-	-
ts1^{II}	0.179[b]	-0.396[b]	-0.183[b]	0.140[b]	-0.138[b]	-0.099[b]	-	-	-
int1^{II}	0.053[b]	0.158[b]	-0.003[b]	0.288[b]	-1.400[b]	-0.388[b]	-	-	-
ic2^{II}	0.015	0.053	-0.001	0.322	-1.665	-0.449	0.324	0.206	-0.322
ts2^{II}	0.045	0.102	-0.002	0.094	-0.067	-0.029	0.318	0.252	-0.311
int2^{II}	0.315	-1.670	-0.469	-	-	-	0.171	0.372	-0.078
ic3^{II}	0.017	0.058	0.001	0.313	-1.623	-0.434	0.321	0.229	-0.314
ts3^{II}	0.048	0.109	-0.002	0.109	-0.125	-0.046	0.310	0.257	-0.295
int3^{II}	0.315	-1.660	-0.468	-	-	-	0.167	0.377	-0.074
ic4^{II}	-	-	-	0.295	-1.513	-0.407	0.331	0.210	-0.333
ts4^{II}	0.048	0.087	-0.004	0.097	-0.087	-0.041	0.314	0.210	-0.303
int4^{II}	0.318	-1.683	-0.473	-	-	-	0.168	0.372	-0.075

[a]H represents H2-H4 in N_2H_4 corresponding to stages 2, 3 and 4 of Pathway II.

[b]H and O represent the H_{eq} and O_{eq} of H_2O in the equatorial plane corresponding to stage 1 of Pathway II.

Table S3 Calculated O_{yl}-H, Np-O_{yl} and N-H WBIs and Mayer Bond Orders of All Species in the Stages 1 and 2 of Pathway III at the B3LYP/6-31g*/ECP60MWB Level of Theory

	WBI			Mayer bond order		
	O_{yl}-H[a]	Np-O_{yl}	N-H[a]	O_{yl}-H[a]	Np-O_{yl}	N-H[a]
ts1^{III}	0.295	0.593	0.444	0.376	0.592	0.355
int1^{III}	0.584	0.436	0.116	0.567	0.423	0.152
int2^{III}	-	1.202	0.718	-	1.095	0.655
ts2^{III}	0.335	0.578	0.381	0.453	0.585	0.253
int3^{III}	0.665	0.403	-	0.643	0.380	-

[a]H represents **H2** (for **ts1^{III}** and **int1^{III}**) and **H4** (for **int2^{III}**, **ts2^{III}** and **int3^{III}**) in N_2H_4.

Table S4 Electron Density [ρ(r), au], Its Laplacian [$\nabla^2\rho$(r), au], and the Total Energy Density [H(r), au] at the BCPs of All Species in the Stages 1 and 2 of Pathway III

	O_{yl}-H[a]			N-H[a]			Np-O_{yl}		
	ρ(r)	∇^2ρ(r)	H（r）	ρ(r)	∇^2ρ(r)	H（r）	ρ(r)	∇^2ρ(r)	H（r）
ts1^{III}	0.087	0.091	-0.023	0.147	-0.319	-0.120	0.058	0.181	-0.002
int1^{III}	0.294	-1.460	-0.423	0.046	0.120	-0.003	0.053	0.188	-0.001
int2^{III}	-	-	-	0.291	-1.415	-0.394	0.160	0.377	-0.065
ts2^{III}	0.045	0.031	-0.006	0.110	-0.181	-0.075	0.053	0.161	-0.002
int3^{III}	0.325	-1.787	-0.498	-	-	-	0.050	0.170	-0.001

[a]H represents H2 (for **ts1^{III}** and **int1^{III}**) and H4 (for **int2^{III}**, **ts2^{III}** and **int3^{III}**) in N_2H_4.

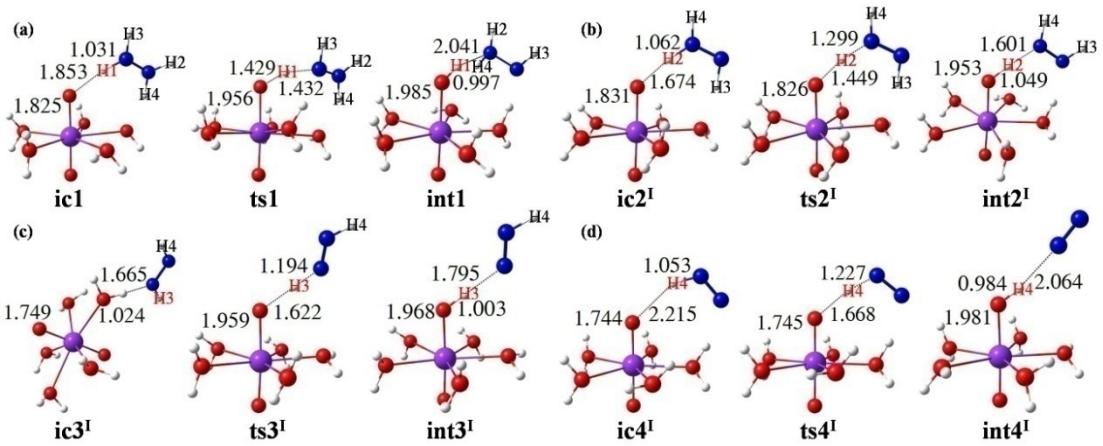

Fig. S1 Structures and selected bond lengths of all species in the Pathway I at the B3LYP/ECP60MWB/6-31g* level of theory (neptunium: purple, oxygen: red, nitrogen: blue, hydrogen: white).

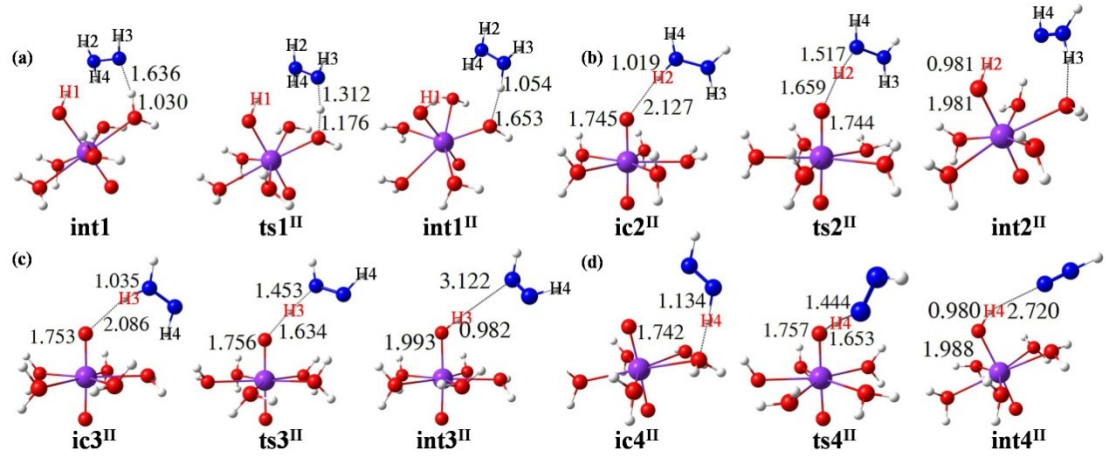

Fig. S2 Structures and selected bond lengths of all species in the Pathway II at the B3LYP/ECP60MWB/6-31g* level of theory.

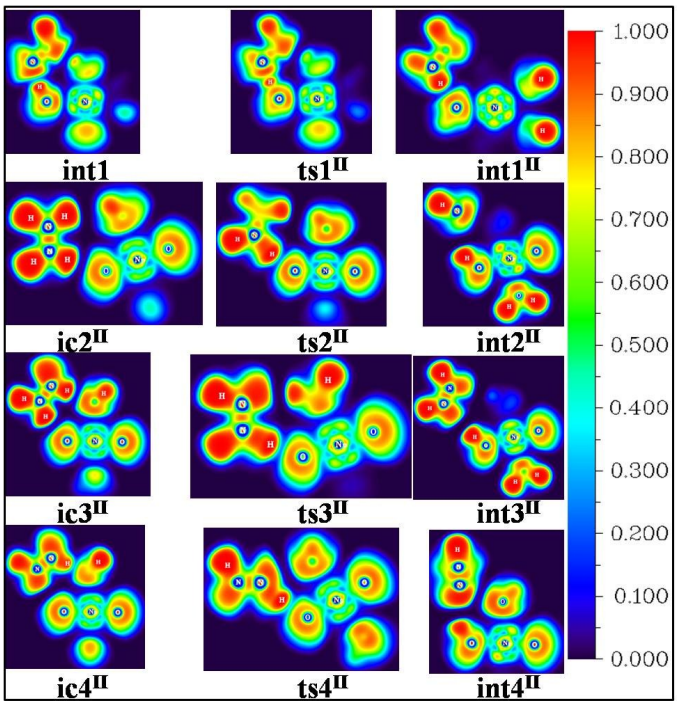

Fig. S3 Two dimensioned ELF contours of all speices on the Np-O_{eq}-N plane for stage 1 and Np-O_{yl}-N plane for stages 2, 3 and 4 of Pathway II.

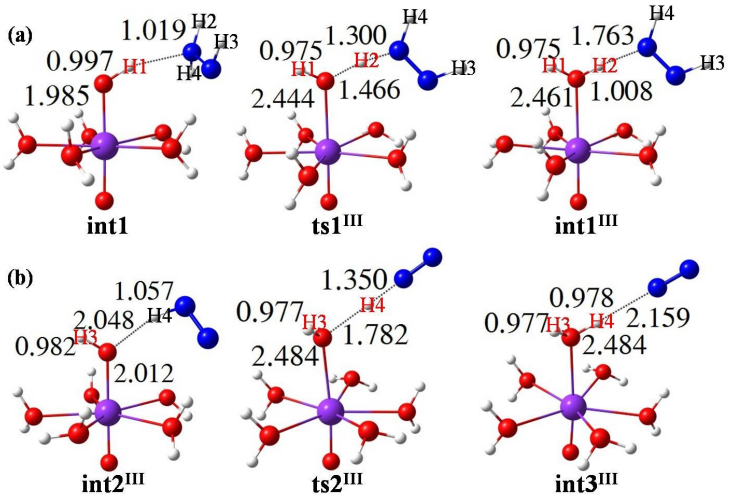

Fig. S4 Structures and selected bond lengths of all species in the stages 1 and 2 of Pathway III at the B3LYP/ECP60MWB/6-31g* level of theory.

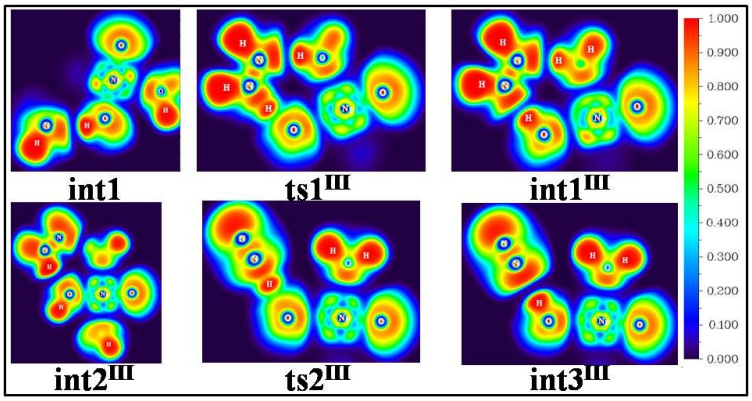

Figure S5 Two dimensioned ELF contours of all species on the Np-O_{yl}-N plane for the transfer of H2 and H4 in stages 1 and 2 of Pathway III.

References

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[2] Z. Cao and K. Balasubramanian, *J. Chem. Phys.*, 2005, **123**, 114309.