Supporting Information

The Role of Neptunium Oxidation States and Coordination in Shaping XANES Spectra at the Np L_3 Absorption Edge

By

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Table S1. Properties and methods for the synthesis of neptunium oxides.

Chemical formula	Color	Syngony and space group	Lattice parameters						Characteristic Raman shifts, cm^{-1}	Synthesis methods
			a, Å	b, Å	c, Å	α,°	β,°	γ,°		
NpO	Black	Cubic, face-centered [1]								Treating of metallic Np with H_2 and impurity of O_2 [2]
NpO_2	Brown or apple-green	Cubic, face-centered Fm3m [3,4]	5.4334± 0.0003	5.4334± 0.0003	5.4334± 0.0003	90	90	90	Γ_8 (431 cm^{-1}), $\Gamma_{25'}$ (466 cm^{-1}), 1LO (580 cm^{-1}), 2LO (1160 cm^{-1}), 3LO (1740 cm^{-1}) [5] T_{2g} (463 cm^{-1}), 1LO (568 cm^{-1}), 2LO (1150 cm^{-1})[6]	Thermal decomposition of Np compounds, e.g. $Np(OH)_4 \cdot xH_2O$ or $NpO_2(OH)_2$ (700-800°C)
Np_2O_5	Brown	Monoclinic [7] P2/c	8.1680	6.5842	9.3127	90	116.089	90	550 and 850 cm^{-1} and smaller at 100 and 250 cm^{-1} [8]	1. Precipitation with O_3 bubbling from molten $LiClO_4$ with NpO_2^+ [9–11] 2. Thermal decomposition of $NpO_3 \cdot H_2O$ [12] 3. Thermal decomposition of NpO_2OH [13] 4. Low-temperature hydrothermal reaction of a $(NpO_2)^+$ solution with calcite crystals [14]

Np_3O_8 or $NpO_{2.64\pm0.3}$	Brown	Orthorhombic, isomorphic to U_3O_8 P-3 [15]								$NpO_2OH\cdot xH_2O$ oxidation with NO_2 (300°C) [15,16]
$NpO_2(OH)_3$ or $NpO_3(OH)$ [17]										Bubbling of O_3 in Np(V) hydroxide suspension [18]
$NpO_3\cdot 2H_2O$ or $NpO_2(OH)_2\cdot H_2O$	Dark yellow	$NpO_2(OH)_2$ orthorhombic, isomorphic to α-$UO_2(OH)_2$ Cmca [19]	4.18(2)	10.17(3)	6.97(3)				786 cm^{-1} [6]	1. Bubbling of O_3 in Np (V) solution in eutectic $LiNO_3/KNO_3$ [10] 2. Bubbling of O_3 in water suspension of Np(V) hydroxide [20]
$NpO_2OH\cdot xH_2O$	Pale-green									Np(VI) in solution was reduced in 0.5M HNO_3 – 0.5M $NaNO_2$ down to (V). The solution was saturated with NH_3 to precipitate $NpO_2OH\cdot xH_2O$ [21]
$Np(OH)_4\cdot xH_2O$	Brown-red or green-gray [21]									

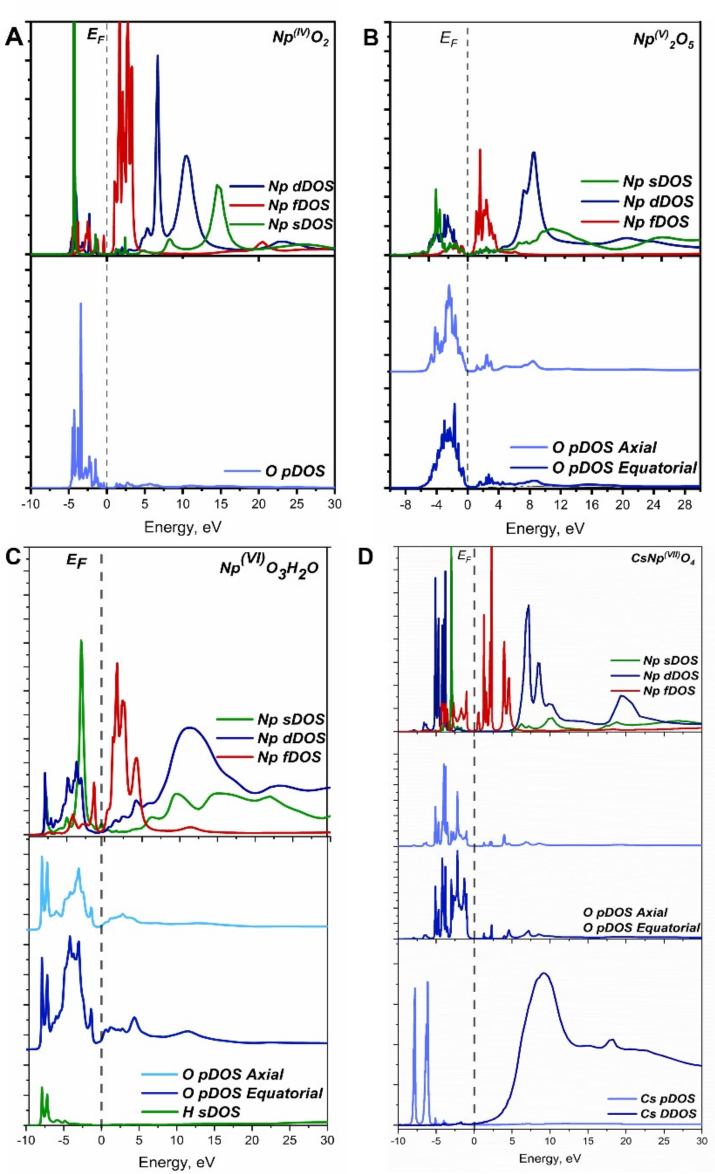

Fig S1 Increased Densities of Electronic States for Compounds NpO_2(A), Np_2O_5(B), NpO_3H_2O(C), $CsNpO_4$ (D)

The quantum-chemical calculations were done at DFT+U level of theory with PAW potentials[22–24]. The exchange-correlation term was treated using the PBE[25] functional with Hubbard corrections in Dudarev form[26]. The U and J parameters were defined as 5 and 0.75 eV correspondingly. The gamma-centered k-points mesh differs from 6*4*4 to 14*14*14 depending on the unit cell size. All the calculations were performed using preliminary geometry optimization at the same level of theory.

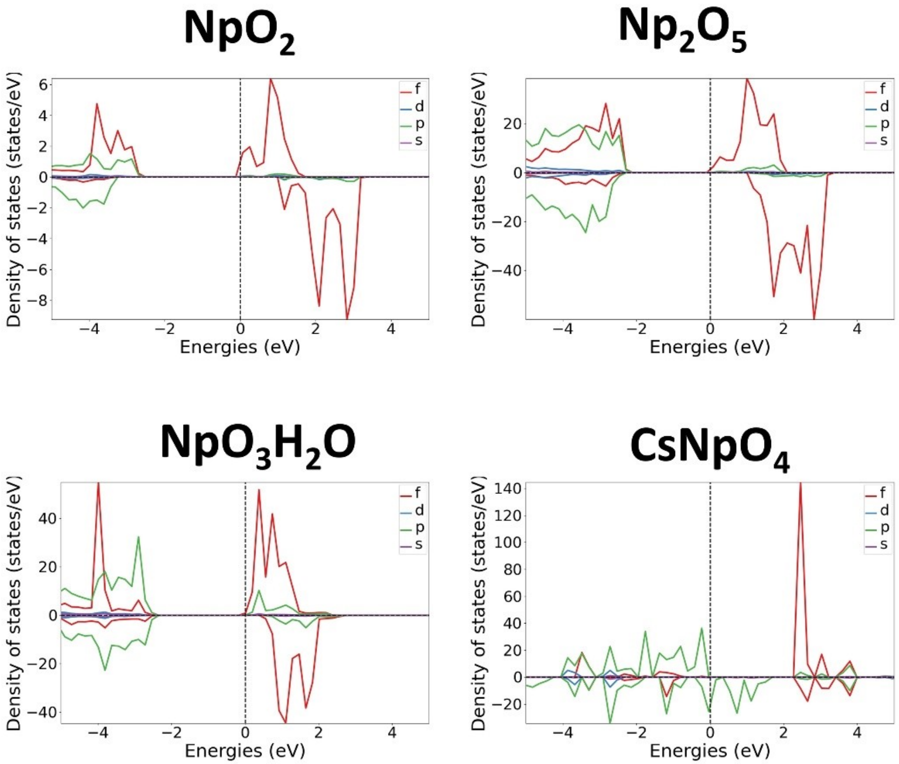

Fig S2 Calculated densities of electronic states (DOS) for neptunium compounds obtained using the DFT+U approach (PBE+U, U = 5 eV, J = 0.75 eV)

Example FDMNES input file S3

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Filout
C:\fdmnes\Np_calculated\NpO2\out\NpO2
Range
-25. 0.1 5. 0.2 10. 0.5 20. 1. 30. 2. 60. 4. 100.
Radius
5
SCF
Gamma_hole
6
Gamma_max
5
Density_all
Edge
L3
E_cut
-1.0
Cif_file
NpO2_mp-2616_symmetrized.cif
Quadrupole
Relativism
Spinorbit
Convolution
End
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