Supplemental Material

The electronic states of U^{4+} in $U(PO_4)Cl$ - An example for angular overlap modeling of $5f^n$ systems

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Table S1. UPO_4Cl. Calculated and observed transition energies, line strengths (I) with assignment of the parental terms for the region between 0 and 26000 cm^{-1} (measured transition are above 6000 cm^{-1}). Irreducible representations are given for split terms of the ground state and for the range 8000 - 11000 cm^{-1}.

Parental term*	$E_{calc.}$ (cm^{-1})	$E_{obs.}$ (cm^{-1})	$I_{calc.}$	$I_{obs.}$	Irred. Repr.
$^3P_2$	24519.		0.5086		
$^3P_2$	23770.		0.0000		
$^3P_2$	23086.		0.2509		
$^3P_2$	22981.	23248	0.0000	0.42	
$^3P_2$	22962.	23043	0.3398	0.25	
$^1I_6$	21629.	22283	0.0000	1.48/0.95	
$^1I_6$	21626.		0.2920		
$^1I_6$	21336.		0.2454		
$^1I_6$	21272.	21527	0.1690	0.32	
$^1I_6$	20846.	21287	0.0000	0.68	
$^1I_6$	20402.	20607	0.0000	0.50	
$^1I_6$	19976.		0.0000		
$^1I_6$	19940.		0.6053		
$^1I_6$	19843.	20327	0.2102	0.54	
$^1I_6$	19716.	19892	0.0000	0.29	
$^1I_6$	19616.	19651	0.0000	0.23	
$^1I_6$	19616.		0.2393		
$^1I_6$	19615.		0.9604		
$^3P_1$	18624.		0.0000		
$^3P_1$	18466.		0.7378		
$^3P_1$	18284.	18691	0.0000	0.72	
$^1G_4$	17306.	17375	0.0519	0.31	
$^1G_4$	17014.	17175	0.2853	0.20	
$^1G_4$	16991.	17015	0.0000	0.28	
$^1G_4$ ($^1D_2$)	16805.		0.0000		
$^1D_2$ ($^1G_4$)	16668.	16665	0.3907	0.11	
$^1D_2$ ($^3P_0$)	16231.	16340	2.8656	0.40	
$^1D_2$	15981.		1.0561		
$^1D_2$	15969.		0.0000		
$^1D_2$	15838.	15940	1.3312	1.16	
$^1G_4$	15805.	15660	0.0000	1.03	
$^1G_4$	15485.		0.0184		
$^1D_2$ ($^1G_4$)	15443.	15379	0.0000	0.33	
$^1G_4$	15377.		0.0000		
$^1G_4$	15263.	14979	0.0506	0.34	
$^1G_4$ ($^3P_0$)	14841.	14584	0.0412	0.26	
$^3H_6$	12860.		0.0000		
$^3H_6$	12843.		0.3089		
$^3H_6$	12769.	13183	0.2845	0.32	
$^3H_6$	12726.	12943	0.0000	0.35	
$^3H_6$	12348.		0.0000		
$^3H_6$	12326.		0.1653		
$^3H_6$	12061.	12188	0.2353	0.17	
$^3H_6$	11865.	12068	0.0000	0.32	
$^3H_6$	11180.	11588	0.7725	0.33	
$^3H_6$	11133.	11348	0.0000	0.26	
$^3H_6$	11123.		0.4676		
$^3H_6$	11021.	11152	0.2035	0.36	
$^3H_6$	10980.		0.0000		
$^3F_4$	10604.	10592	0.0000	0.30	Γ_3
$^3F_4$	10488.		0.6577		Γ_4
$^3F_4$	10414.		0.7357		Γ_1
$^3F_4$	10093.	10272	0.0000	0.31	Γ_2
$^3F_4$ ($^3F_3$)	9774.		0.0000		Γ_3
$^3F_3$	9738.	9592	0.0206	0.21	Γ_4
$^3F_3$	9484.		0.0000		Γ_2
$^3F_3$	9435.		0.0000		Γ_2
$^3F_4$	9349.		0.5060		Γ_1
$^3F_3$ ($^3F_4$)	9199.	9316	0.0000	1.70	Γ_3
$^3F_4$ ($^3H_5$)	9108.	9200	2.0029	1.50	Γ_2
$^3F_3$ ($^3F_4$)	9100.	9196	0.0000	1.45	Γ_4
$^3F_3$	9072.	9076	4.0179	1.26	Γ_1

$^3F_4$ ($^3F_3$)	9001.		2.2366		Γ_4
$^3F_3$ ($^3F_4$)	8825.		0.0000		Γ_3
^3F	8571.	8556	1.2043	0.77	Γ_1
$^3H_5$	7532.	7876	0.0000	0.67	
$^3H_5$	7308.	7480	0.7517	0.92	
$^3H_5$	7082.	7280	0.0000	1.09	
$^3H_5$	7049.		0.5814		
$^3H_5$	7048.		0.0000		
$^3H_5$	7031.	7040	0.7799	1.24	
$^3H_5$	6599.		2.1497		
$^3H_5$	6515.	6520	0.0000	0.72	
$^3H_5$	6287.		0.0000		
$^3H_5$	6287.	6080	1.1403	0.70	
$^3H_5$	6050.		0.0000		
$^3F_2$	4914.		2.6720		
$^3F_2$	4779.		2.8672		
$^3F_2$	4730.		0.0000		
$^3F_2$	4551.		2.1666		
$^3F_2$	4542.		0.0000		
$^3H_4$	2117.		1.3616		Γ_4
$^3H_4$	2015.		0.0000		Γ_3
$^3H_4$	1656.		0.8601		Γ_1
$^3H_4$	1370.		0.0000		Γ_2
$^3H_4$	852.		0.1315		Γ_1
$^3H_4$	730.		0.0000		Γ_3
$^3H_4$	690.		0.0000		Γ_2
$^3H_4$	681.		0.0169		Γ_4
$^3H_4$	0.		0.0000		Γ_1

Table S2. Calculated and observed transition energies for the chromophore $[U^{IV}Cl_6]$ in Cs_2ZrCl_6.

$E_{calc.}$ (BonnMag) (cm^{-1})	$E_{calc.}$ [Ref. 23] (cm^{-1})	$E_{obs.}$ (cm^{-1})
860	859	915
1178	1177	
2297	2296	
4855	4860	
5020	5024	5060
6277	6272	6343
7036	7032	
7109	7107	
7794	7791	8197
8274	8278	8469
9236	9236	
9299	9299	
9736	9735	9540
9898	9898	
10051	10052	10065
10910	10908	
11309	11305	11176
11336	11334	
12072	12066	12128
12803	12798	12878
13158	13154	
13169	13165	12984
14588	14600	14789
15517	15522	15213
15608	15616	15754
16289	16307	
16826	16849	16797
17035	17049	
17536	17540	
18832	18857	18823
19964	19980	
20015	20034	
20066	20083	
21051	21073	
21775	21796	
21953	21975	
23307	23327	23399
24740	24758	24700
41550	41621	

Table S3. AOM (BonnMag) input file for the chromophore [$U^{IV}O_6$] in UP_2O_7 (real geometry).

```
TITLE U4+ in UP2O7
CONF 3 2
CELL 8.6311 8.6311 8.6311 90.0 90.0 90.0
MULT 1
U   0.0 0.0 0.0
O  -0.0513  0.2455  0.0679
O  -0.0513 -0.2455 -0.0679
O   0.2455  0.0679  -0.0513
O  -0.0679  0.0513  -0.2455
O  -0.2455 -0.0679  0.0513
O   0.0679 -0.0513  0.2455
XREF  2 1 4
LGND 1 1 2 1 4
LGND 2 1 3 1 4
LGND 3 1 4 1 2
LGND 4 1 5 1 2
LGND 5 1 6 1 2
LGND 6 1 7 1 2
END
```

Table S4. AOM (BonnMag) input file for the chromophore [$U^{IV}O_6$] (ideal octahedron).

```
TITLE U4+ in UP2O7 (ideal)
CONF 3 2
CELL 8.6311 8.6311 8.6311 90.0 90.0 90.0
MULT 1
U    0.0  0.0  0.0
O    0.0  0.0  0.5
O    0.0  0.0 -0.5
O    0.0  0.5  0.0
O    0.0 -0.5  0.0
O    0.5  0.0  0.0
O   -0.5  0.0  0.0
XREF  2 1 4
LGND 1 1 2 1 5
LGND 2 1 3 1 4
LGND 3 1 4 1 2
LGND 4 1 5 1 2
LGND 5 1 6 1 2
LGND 6 1 7 1 2
END
```

Table S5. AOM parameters for the chromophore [$U^{IV}O_6$] (ideal octahedron) and distorted geometry in UP_2O_7.

Slater-Condon-Shortley parameters (cm^{-1})				
$F_2 = 190.9$	$F_4 = 33.74$	$F_6 = 3.99675$ ($\beta = F_2 / F_{2,\text{f.i.}} = 0.82$ [27])		
Slater-Condon-Shortley parameters of the free U^{4+} ion (cm^{-1}) [27]				
$F_{2,\text{f.i.}} = 234.73$	$F_{4,\text{f.i.}} = 41.35$	$F_{6,\text{f.i.}} = 4.10$		
Spin-orbit coupling constant (cm^{-1})				
$\zeta = 1797.02$				
Interaction parameters e_m(U-O) (m: σ, π)				
Ligand	**Distance (Å)**	**e_σ (cm^{-1})**	**$e_{\pi,\text{iso}}$ (cm^{-1})**	**e_π / e_σ**
O1	2.243	1832	458	0.25
Judd-Ofelt parameters (10^{-24} m^2)				
$\Omega_2 = 1.078$	$\Omega_4 = 2.014$	$\Omega_6 = 0.4529$		

Table S6. AOM (BonnMag) input file for $U_2O(PO_4)_2$ ($[U^{IV}O_7]$ chromophore).

```
TITLE U4+ in (U2O)(PO4)2
CONF 3 2
CELL 7.0883 9.037 12.702 90.0 90.0 90.0
MULT 1
U   0.0 0.20793 0.42983
O1 -0.3305 0.1823 0.4148
O1  0.3305 0.1823 0.4148
O1 -0.1695 0.3177 0.5852
O1  0.1695 0.3177 0.5852
O2 0.0 0.1428 0.2582
O3 0.0 0.0 0.5
O4 0.0 0.4432 0.3754
XREF  8 1 2
LGND 1 1 2 1 8
LGND 2 1 3 1 8
LGND 3 2 4 1 8
LGND 4 2 5 1 8
LGND 5 3 6 1 8
LGND 6 4 7 1 2
LGND 7 5 8 1 2
END
```

Table S7. AOM parameters for the $[U^{IV}O_7]$ chromophore in $U_2O(PO_4)_2$.

Slater-Condon-Shortley parameters (cm^{-1})

$F_2 = 190.9$ $F_4 = 33.74$ $F_6 = 3.99675$ ($\beta = F_2 / F_{2,\text{f.i.}} = 0.82$ [27])

Slater-Condon-Shortley parameters of the free U^{4+} ion (cm^{-1}) [27]

$F_{2,\text{f.i.}} = 234.73$ $F_{4,\text{f.i.}} = 41.35$ $F_{6,\text{f.i.}} = 4.10$

Spin-orbit coupling constant (cm^{-1})

$\zeta = 1797.02$

Interaction parameters e_m(U-O) (m: σ, π)

Ligand	Distance (Å)	e_σ (cm^{-1})	$e_{\pi,\text{iso}}$ (cm^{-1})	e_π / e_σ
O3	2.080	3107	777	0.25
O4	2.236	1873	468	0.25
O2	2.258	1749	437	0.25
O1	2.362	1276	319	0.25
O1'	2.514	825	206	0.25

Judd-Ofelt parameters (10^{-24} m^2)

$\Omega_2 = 1.078$ $\Omega_4 = 2.014$ $\Omega_6 = 0.4529$

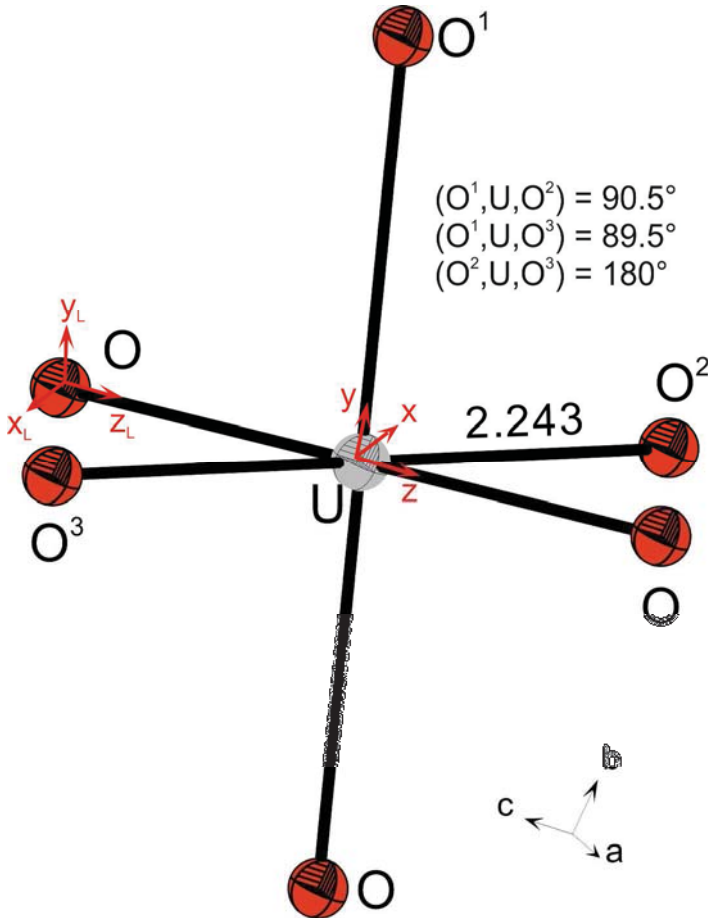

Figure S1 ORTEP representation of the [$U^{IV}O_6$] chromophore in UP_2O_7 given with coordinate systems for the central atom (global coordinate system) and one ligand as example (index L).

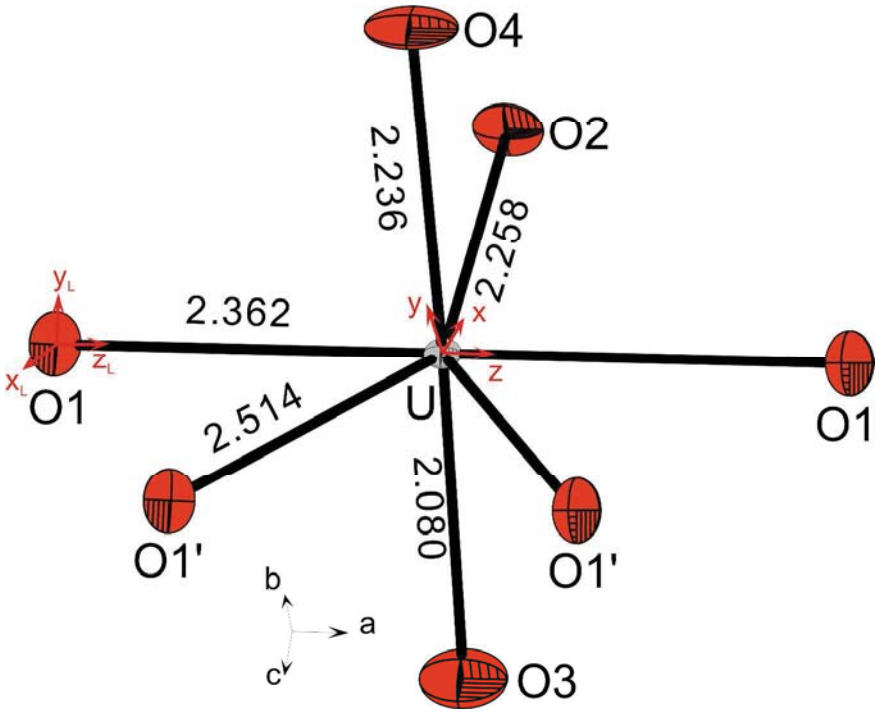

Figure S2 ORTEP representation of the [$U^{IV}O_7$] chromophore in $U_2O(PO_4)_2$ given with coordinate systems for the central atom (global coordinate system) and one ligand as example (index L).