Supplementary Material for PCCP

Supporting information for: Effects of the first hydration sphere and the bulk solvent on the spectra of the f^2 isoelectronic actinide compounds: U^{4+}, NpO_2^+, and PuO_2^{2+}

Cécile Danilo,[†] Jean-Pierre Flament,[†] Valérie Vallet,[*,†] and Ulf Wahlgren[‡]

Université des Sciences et Technologies de Lille 1, Laboratoire PhLAM, CNRS UMR 8523, CERLA, CNRS FR 2416, Bât P5, 59655 Villeneuve d'Ascq Cedex, France, and Department of Physics, Stockholm University, AlbaNova University Centre, 106 91 Stockholm, Sweden and NORDITA, AlbaNova University Centre, 106 91 Stockholm, Sweden

E-mail: valerie.vallet@univ-lille1.fr

[*]To whom correspondence should be addressed

[†]Université des Sciences et Technologies de Lille 1, Laboratoire PhLAM, CNRS UMR 8523, CERLA, CNRS FR 2416, Bât P5, 59655 Villeneuve d'Ascq Cedex, France

[‡]Department of Physics, Stockholm University, AlbaNova University Centre, 106 91 Stockholm, Sweden and NORDITA, AlbaNova University Centre, 106 91 Stockholm, Sweden

List of Tables

Tables

Table 1: Bond distances in Angstroms of hydrated $[U(H_2O)_8]^{4+}$, $[NpO_2(H_2O)_5]^{+}$, and $[PuO_2(H_2O)_5]^{2+}$ complexes.

Complex	$R(An-O_{yl})$	$R(An-OH_2)$
$[U(H_2O)_8]^{4+}$	...	2.475
$[NpO_2(H_2O)_5]^{+}$	1.790	2.590
$[PuO_2(H_2O)_5]^{2+}$	1.719	2.490 ± 0.005

Table 2: Cartesian coordinates of $[U(H_2O)_8]^{4+}$ in Angstroms.

Atom	x	y	z
U	0.000000	0.000000	0.000000
O	0.000000	2.003970	1.452183
O	0.000000	-2.003970	-1.452183
O	-2.003970	0.000000	1.452183
O	2.003970	0.000000	-1.452183
O	0.000000	-2.003970	1.452183
O	0.000000	2.003970	-1.452183
O	2.003970	0.000000	1.452183
O	-2.003970	0.000000	-1.452183
H	-0.762458	2.515692	1.787052
H	0.762458	-2.515692	-1.787052
H	0.762458	2.515692	1.787052
H	-0.762458	-2.515692	-1.787052
H	-2.515692	-0.762458	1.787052
H	2.515692	0.762458	-1.787052
H	-2.515692	0.762458	1.787052
H	2.515692	-0.762458	-1.787052
H	0.762458	-2.515692	1.787052
H	-0.762458	2.515692	-1.787052
H	-0.762458	-2.515692	1.787052
H	0.762458	2.515692	-1.787052
H	2.515692	0.762458	1.787052
H	-2.515692	-0.762458	-1.787052
H	2.515692	-0.762458	1.787052
H	-2.515692	0.762458	-1.787052

Table 3: Cartesian coordinates of $[NpO_2(H_2O)_5]^+$ in Angstroms.

Atom	x	y	z
Np	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.789671
O	0.000000	0.000000	-1.789727
O	-2.462823	-0.800220	-0.000558
O	0.000000	-2.589565	-0.000558
O	-1.522109	2.095002	-0.000558
O	1.522108	2.095003	-0.000558
O	2.462823	-0.800219	-0.000558
H	-3.094226	-0.690458	-0.720272
H	-2.911034	-1.258452	0.719042
H	-0.299504	-3.156147	-0.720272
H	0.297300	-3.157441	0.719042
H	-1.612833	2.729421	-0.720272
H	-2.096418	2.379675	0.719042
H	2.909122	-1.260148	-0.720272
H	3.094775	-0.692954	0.719042
H	2.097440	2.377333	-0.720272
H	1.615376	2.729172	0.719042

Table 4: Cartesian coordinates of $[PuO_2(H_2O)_5]^{2+}$ in Angstroms.

Atom	x	y	z
Pu	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.719712
O	-0.000957	0.003909	1.719066
O	1.438517	2.029018	0.004841
O	2.379105	-0.738238	-0.006265
O	-1.561727	1.938500	-0.004294
O	-2.309734	-0.924121	-0.004562
O	0.108563	-2.492715	-0.003283
H	1.492156	2.699449	0.702664
H	2.069504	2.289159	-0.683324
H	3.049829	-0.537295	0.663080
H	2.802650	-1.298773	-0.673232
H	-2.192985	2.169668	0.694006
H	-1.664317	2.601316	-0.704116
H	0.550419	-3.049073	0.654854
H	-0.276886	-3.086036	-0.664704
H	-2.692455	-1.507515	0.667668
H	-2.987847	-0.792107	-0.683952

Table 5: Spectrum of $[U(H_2O)_8]^{4+}$ in gas-phase computed at the SO-CASPT2 level. Energies are in cm^{-1}.

Energy	Contributions of U^{4+} SO states
0	46% $^3H_4$
210	46% $^3H_4$
309	44% $^3H_4$
316	44% $^3H_4$
1277	43% $^3H_4$
1345	44% $^3H_4$
1464	45% $^3H_4$
5114	33% $^3F_2$ + 13% $^3H_5$
5286	20% $^3F_2$ + 29% $^3H_5$
5325	9% $^3H_5$ + 37% $^3F_2$
5428	30% $^3F_2$ + 16% $^3H_5$
6495	52% $^3H_5$
6678	45% $^3H_5$
6804	14% $^3F_2$ + 35% $^3H_5$
6808	45% $^3H_5$
7073	49% $^3H_5$
7452	21% $^3H_5$ + 23% $^3F_2$
7679	37% $^3H_5$
7909	45% $^3H_5$
9846	45% $^3F_3$
9942	30% $^3F_3$ + 17% $^3H_6$
10017	12% $^3H_6$ + 35% $^3F_3$
10734	35% $^3F_3$
10747	11% $^3H_6$ + 15% $^3F_4$ + 15% $^1G_4$
11092	30% $^3F_3$ + 10% $^3H_6$

Table 5: continue

Energy	Contributions of U^{4+} SO states
11240	8% $^3F_3$ + 9% $^1G_4$ + 9% $^3F_4$ + 23% $^3H_6$
11301	13% $^3F_4$ + 9% $^3F_3$ + 13% $^1G_4$ + 13% $^3H_6$
11625	14% $^3F_4$ + 14% $^1G_4$ + 19% $^3H_6$
11787	11% $^1G_4$ + 22% $^3H_6$ + 11% $^3F_4$
11955	16% $^3H_6$ + 16% $^3F_3$ + 9% $^3F_4$ + 9% $^1G_4$
12047	15% $^3F_4$ + 15% $^1G_4$ + 18% $^3H_6$
12310	11% $^3F_4$ + 23% $^3H_6$ + 11% $^1G_4$
12454	36% $^3H_6$ + 9% $^3F_3$
12501	32% $^3H_6$
13042	26% $^3H_6$ + 10% $^3F_4$ + 10% $^1G_4$
13130	31% $^3H_6$
13626	10% $^3F_4$ + 10% $^1G_4$ + 26% $^3H_6$
13717	34% $^3H_6$
14038	39% $^3H_6$
14625	37% $^3H_6$
15237	38% $^3H_6$
18727	21% $^3F_4$ + 17% $^1G_4$
18935	11% $^1D_2$ + 17% $^3F_4$ + 14% $^1G_4$
19331	44% $^3P_0$
19411	17% $^3F_4$ + 13% $^1G_4$ + 13% $^1D_2$
19632	22% $^3F_4$ + 18% $^1G_4$
19884	14% $^1G_4$ + 11% $^1D_2$ + 17% $^3F_4$
19891	26% $^3F_4$ + 22% $^1G_4$
20117	10% $^3P_2$ + 21% $^1D_2$
20322	16% $^1G_4$ + 19% $^3F_4$
20431	9% $^3P_2$ + 18% $^1D_2$ + 9% $^1G_4$ + 11% $^3F_4$

Table 5: continue

Energy	Contributions of U^{4+} SO states
20799	22% $^1D_2$ + 11% $^3P_2$
21155	19% $^1G_4$ + 23% $^3F_4$
22265	50% $^3P_1$
22632	51% $^3P_1$
26586	43% $^1I_6$
26623	48% $^1I_6$
26642	20% $^3P_2$ + 23% $^1I_6$
27353	28% $^3P_2$ + 11% $^1D_2$ + 12% $^1I_6$
27638	46% $^1I_6$
27828	50% $^1I_6$
28012	11% $^1D_2$ + 29% $^3P_2$ + 12% $^1I_6$
28143	38% $^1I_6$ + 9% $^3P_2$
28401	22% $^1I_6$ + 21% $^3P_2$ + 8% $^1D_2$
29409	50% $^1I_6$
29589	43% $^1I_6$
30731	46% $^1I_6$
31217	12% $^3P_2$ + 30% $^1I_6$
32342	30% $^1I_6$ + 12% $^3P_2$
48323	48% $^1S_0$

Table 6: Absorption spectrum of $[U(H_2O)_8]^{4+}$ in PCM computed at the SO-CASPT2 level (PCM equilibrated on the ground-state). Energies are in cm^{-1}.

Energy	Contributions of U^{4+} SO states
0	47% $^3H_4$
150	47% $^3H_4$
157	47% $^3H_4$
468	45% $^3H_4$
504	45% $^3H_4$
1288	44% $^3H_4$
1301	45% $^3H_4$
1311	45% $^3H_4$
1446	46% $^3H_4$
5174	12% $^3H_5$ + 35% $^3F_2$
5184	11% $^3H_5$ + 35% $^3F_2$
5350	29% $^3H_5$ + 21% $^3F_2$
5389	37% $^3F_2$ + 9% $^3H_5$
5442	16% $^3H_5$ + 31% $^3F_2$
6377	53% $^3H_5$
6688	50% $^3H_5$
6703	50% $^3H_5$
6818	45% $^3H_5$
6826	45% $^3H_5$
6920	13% $^3F_2$ + 36% $^3H_5$
7112	49% $^3H_5$
7413	23% $^3F_2$ + 23% $^3H_5$
7732	38% $^3H_5$
7788	45% $^3H_5$
7797	45% $^3H_5$

Table 6: continue

Energy	Contributions of U^{4+} SO states
9848	45% $^3F_3$
9853	45% $^3F_3$
9919	35% $^3F_3$ + 13% $^3H_6$
10168	38% $^3F_3$ + 11% $^3H_6$
10787	40% $^3F_3$
10900	13% $^3H_6$ + 16% $^3F_4$ + 16% $^1G_4$
11159	33% $^3F_3$ + 12% $^3H_6$
11163	12% $^3H_6$ + 33% $^3F_3$
11317	23% $^3H_6$ + 10% $^1G_4$ + 10% $^3F_4$
11321	11% $^3H_6$ + 15% $^3F_4$ + 15% $^1G_4$
11326	11% $^3H_6$ + 15% $^3F_4$ + 15% $^1G_4$
11748	14% $^3F_4$ + 14% $^1G_4$ + 20% $^3H_6$
11852	11% $^3F_4$ + 11% $^1G_4$ + 25% $^3H_6$
11872	10% $^1G_4$ + 26% $^3H_6$ + 10% $^3F_4$
11899	11% $^1G_4$ + 11% $^3F_4$ + 16% $^3H_6$ + 12% $^3F_3$
12081	23% $^3H_6$ + 13% $^1G_4$ + 13% $^3F_4$
12337	33% $^3H_6$
12346	24% $^3H_6$ + 10% $^1G_4$ + 10% $^3F_4$
12363	32% $^3H_6$
12371	31% $^3H_6$
12994	10% $^3F_4$ + 10% $^1G_4$ + 26% $^3H_6$
13116	29% $^3H_6$
13137	28% $^3H_6$
13676	27% $^3H_6$ + 11% $^1G_4$ + 11% $^3F_4$
13833	36% $^3H_6$
14013	38% $^3H_6$

Table 6: continue

Energy	Contributions of U^{4+} SO states
14544	38% $^3H_6$
14546	38% $^3H_6$
15146	8% $^3F_3$ + 40% $^3H_6$
18903	21% $^3F_4$ + 17% $^1G_4$
19039	18% $^3F_4$ + 15% $^1G_4$ + 10% $^1D_2$
19042	10% $^1D_2$ + 15% $^1G_4$ + 18% $^3F_4$
19381	18% $^3F_4$ + 15% $^1G_4$ + 11% $^1D_2$
19399	45% $^3P_0$
19647	21% $^3F_4$ + 17% $^1G_4$
19946	27% $^3F_4$ + 22% $^1G_4$
20080	15% $^3F_4$ + 12% $^1D_2$ + 13% $^1G_4$
20109	14% $^1D_2$ + 11% $^1G_4$ + 14% $^3F_4$
20212	22% $^1D_2$ + 11% $^3P_2$
20372	10% $^3F_4$ + 20% $^1D_2$ + 10% $^3P_2$
20458	16% $^1G_4$ + 20% $^3F_4$
20512	22% $^3F_4$ + 18% $^1G_4$
20749	10% $^3P_2$ + 22% $^1D_2$
21286	24% $^3F_4$ + 20% $^1G_4$
22317	51% $^3P_1$
22329	51% $^3P_1$
22630	52% $^3P_1$
26828	20% $^3P_2$ + 24% $^1I_6$
26838	20% $^3P_2$ + 24% $^1I_6$
27057	10% $^3P_2$ + 38% $^1I_6$
27070	47% $^1I_6$
27424	16% $^1I_6$ + 26% $^3P_2$ + 10% $^1D_2$

Table 6: continue

Energy	Contributions of U^{4+} SO states
27654	50% $^1I_6$
27708	51% $^1I_6$
27733	51% $^1I_6$
28091	27% $^3P_2$ + 10% $^1D_2$ + 15% $^1I_6$
28223	12% $^3P_2$ + 35% $^1I_6$
28265	24% $^1I_6$ + 20% $^3P_2$
29337	50% $^1I_6$
29608	48% $^1I_6$
29659	47% $^1I_6$
30776	47% $^1I_6$
31069	15% $^3P_2$ + 27% $^1I_6$
31111	14% $^3P_2$ + 28% $^1I_6$
32195	12% $^3P_2$ + 31% $^1I_6$
48357	49% $^1S_0$

Table 7: Emission spectrum of $[U(H_2O)_8]^{4+}$ in PCM computed at the SO-CASPT2 level (PCM equilibrated on the highest singlet state). Energies are in cm^{-1}.

Transition energy from the ground state	Emission[1] from $^1S_0$	Contributions of U^{4+} SO states
0	37362	47% $^3H_4$
104	37257	47% $^3H_4$
106	37362	47% $^3H_4$
424	36938	45% $^3H_4$
539	36938	45% $^3H_4$
1078	36284	45% $^3H_4$
1154	36208	45% $^3H_4$
1166	36196	45% $^3H_4$
1259	36103	46% $^3H_4$
4923	32439	39% $^3F_2$
4928	32434	38% $^3F_2$
5093	32269	23% $^3H_5$ + 26% $^3F_2$
5143	32269	40% $^3F_2$
5194	32168	37% $^3F_2$ + 10% $^3H_5$
6476	30886	52% $^3H_5$
6808	30554	43% $^3H_5$
6850	30512	50% $^3H_5$
6858	30504	49% $^3H_5$
6910	30452	43% $^3H_5$
6911	30451	47% $^3H_5$
6958	30451	15% $^3F_2$ + 32% $^3H_5$
7008	30354	49% $^3H_5$
7725	29637	42% $^3H_5$
7899	29463	46% $^3H_5$

[1] $^1S_0$ shifted by -7687 cm^{-1} to match the $^1S_0$ experimental absorption energy

Table 7: continue

Transition energy from the ground state	Emission[1] from $^1S_0$	Contributions of U^{4+} SO states
7901	29461	46% $^3H_5$
9569	27793	34% $^3F_3$
9573	27788	35% $^3F_3$
9750	27788	36% $^3F_3$ + 8% $^3H_6$
10036	27611	10% $^3H_6$ + 25% $^3F_3$
10070	27291	17% $^1G_4$ + 17% $^3F_4$ + 11% $^3F_3$
10078	27284	17% $^1G_4$ + 11% $^3F_3$ + 17% $^3F_4$
10133	27229	9% $^3H_6$ + 18% $^1G_4$ + 18% $^3F_4$
10262	27099	14% $^1G_4$ + 15% $^3F_3$ + 14% $^3F_4$
10574	26788	22% $^3F_4$ + 22% $^1G_4$
10775	26587	10% $^1G_4$ + 10% $^3F_4$ + 19% $^3F_3$ + 10% ^3H
10789	26573	17% $^3F_4$ + 17% $^1G_4$ + 8% $^3H_6$
10855	26507	9% $^3H_6$ + 16% $^3F_4$ + 16% $^1G_4$
11083	26279	22% $^1G_4$ + 22% $^3F_4$
11183	26178	8% $^3F_4$ + 34% $^3F_3$
11204	26157	37% $^3F_3$
11215	26147	37% $^3F_3$
12070	25292	48% $^3H_6$
12118	25244	42% $^3H_6$
12137	25225	46% $^3H_6$
12151	25211	43% $^3H_6$
12457	24904	44% $^3H_6$
12778	24584	37% $^3H_6$
12828	24534	38% $^3H_6$
12841	24521	38% $^3H_6$

[1] $^1S_0$ shifted by -7687 cm^{-1} to match the $^1S_0$ experimental absorption energy

Table 7: continue

Transition energy from the ground state	Emission[1] from $^1S_0$	Contributions of U^{4+} SO states
13371	23991	42% $^3H_6$
13545	23817	46% $^3H_6$
13886	23476	44% $^3H_6$
13901	23461	44% $^3H_6$
14641	22721	9% $^3F_3$ + 42% $^3H_6$
16978	20384	13% $^3F_4$ + 11% $^1G_4$ + 15% $^1D_2$
17069	20293	13% $^1D_2$ + 13% $^1G_4$ + 16% $^3F_4$
17301	20061	12% $^1D_2$ + 13% $^1G_4$ + 16% $^3F_4$
17627	19735	9% $^3P_2$ + 19% $^1D_2$ + 9% $^3F_4$
17684	19678	15% $^1G_4$ + 19% $^3F_4$ + 10% $^1D_2$
17826	19536	16% $^1G_4$ + 19% $^3F_4$
17911	19451	15% $^1G_4$ + 9% $^1D_2$ + 18% $^3F_4$
18009	19353	10% $^1D_2$ + 11% $^1G_4$ + 13% $^3F_4$ + 9% $^3P_0$
18171	19191	27% $^3F_4$ + 22% $^1G_4$
18385	18976	19% $^3F_4$ + 9% $^1D_2$ + 15% $^1G_4$
18553	18809	16% $^3P_0$ + 12% $^1D_2$
18647	18715	21% $^3F_4$ + 17% $^1G_4$
18724	18638	17% $^1G_4$ + 21% $^3F_4$
18735	18627	8% $^3P_2$ + 9% $^3F_4$ + 17% $^1D_2$
19304	18058	15% $^3P_0$ + 14% $^1G_4$ + 18% $^3F_4$
21391	15971	51% $^3P_1$
21488	15874	50% $^3P_1$
22021	15340	52% $^3P_1$
23831	13531	49% $^1I_6$
23892	13469	48% $^1I_6$

[1] $^1S_0$ shifted by -7687 cm^{-1} to match the $^1S_0$ experimental absorption energy

Table 7: continue

Transition energy from the ground state	Emission[1] from $^1S_0$	Contributions of U^{4+} SO states
24249	13113	46% $^1I_6$
24265	13097	49% $^1I_6$
24326	13036	51% $^1I_6$
24508	12854	12% $^3P_2$ + 33% $^1I_6$
24519	12843	46% $^1I_6$
24688	12674	13% $^3P_2$ + 30% $^1I_6$
25468	11894	27% $^1I_6$ + 17% $^3P_2$
25802	11560	49% $^1I_6$
25821	11541	49% $^1I_6$
25938	11424	13% $^1D_2$ + 34% $^3P_2$
25992	11370	49% $^1I_6$
26419	10943	35% $^3P_2$ + 14% $^1D_2$
27434	9928	47% $^1I_6$
28554	8807	19% $^1I_6$ + 21% $^3P_2$ + 8% $^1D_2$
28689	8673	23% $^3P_2$ + 9% $^1D_2$ + 17% $^1I_6$
29320	8042	22% $^1I_6$ + 19% $^3P_2$
45048	0	48% $^1S_0$

$^1S_0$ shifted by -7687 cm^{-1} to match the $^1S_0$ experimental absorption energy