Supplementary Information

Probing the local coordination of hexavalent uranium and the splitting of 5f orbitals induced by chemical bonding.

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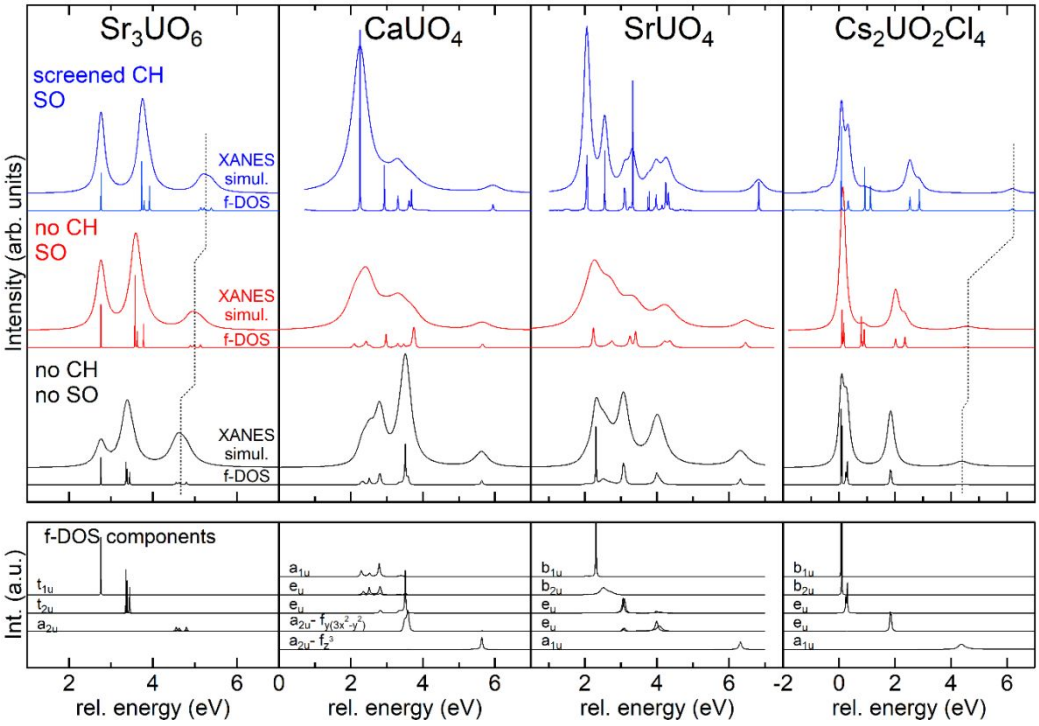

Figure S1: Main panel: convoluted XANES simulations and corresponding total f-DOS for the four samples under investigation. In black, simulation obtained neglecting spin-orbit coupling of the valence states (SO) and core-hole potential (CH). In red, simulations with SO included. In blue, simulations with both SO and CH included. For all samples the CH was fully screened except for $Cs_2UO_2Cl_4$ for which a screening of 60% was applied. Bottom panel: the components of the f-DOS extracted from simulations without SO and CH are shown and labelled according to the irreducible representations of the corresponding point group. We notice that the XANES simulation for the M_4 edge selects only the $f_{5/2}$-DOS. This is the origin of different intensities between features of the total f-DOS and the XANES simulations.

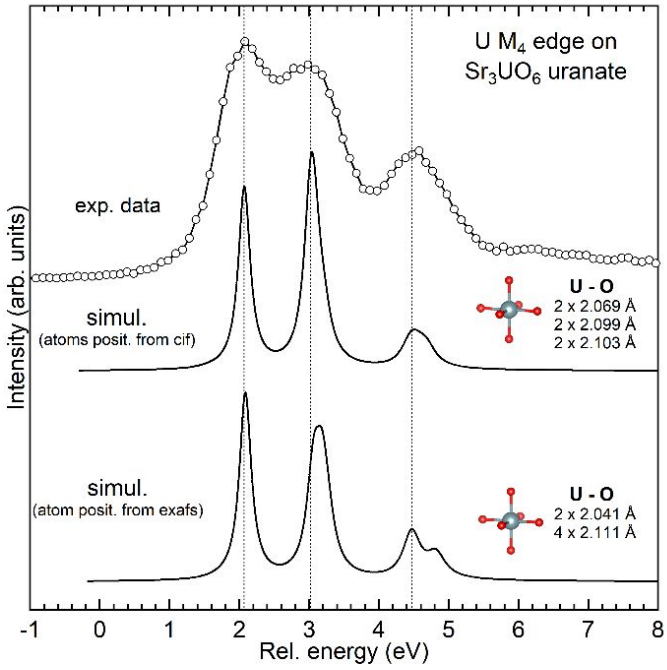

Figure S2: XANES simulations obtained with atomic coordinates from the XRD crystal structure of Sr_3UO_6 (ICDS databse) and with U – O bond lengths modified according to EXAFS measurements from Prieur at al.[1] The relative intensity of peak A improves when the local distortion measured by EXAFS is included. Moreover, the asymmetry of peak C also improves.

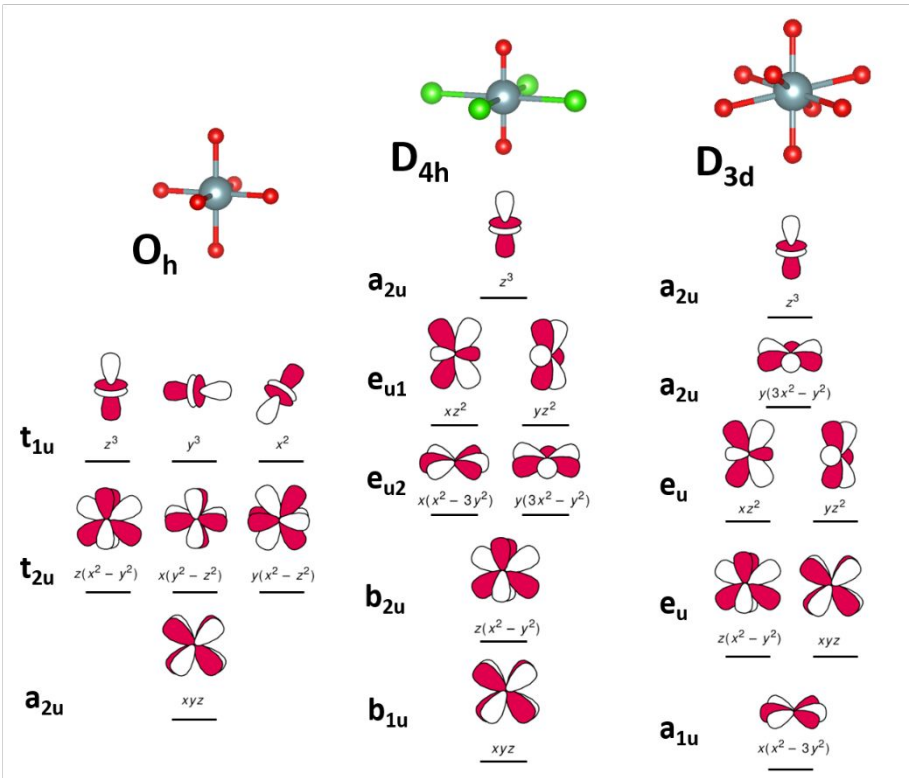

Figure S3: splitting of f-orbital under O_h, D_{4h} and D_{3d} symmetries.

Table S1: energies of the symmetry split 5f orbital obtained from CF simulations reported in Figure 5 and FDMNES simulations without CH and spin-orbit included. All energy values are in eV. The parameter Me_u, used ion CF calculations, quantifies the mixing of the two e_u groups in D_{4h} symmetry.

sample	approach	b_{1u}	b_{2u}	e_{u2}	e_{u1}	a_{2u}	Me_u
$Cs_2UO_2Cl_4$	CF	0.0	-0.2	0.6	1.8	5.9	0.4
	FDMNES	0.0	0.03	0.14-0.23	1.75-1.79	4.33	-
$SrUO_4$	CF	0.0	0.05	0.9	1.9	3.9	0.4
	FDMNES	0.0	0.21	0.75-0.79	1.69-1.78	4.01	-
		a_{2u}	t_{2u}	t_{1u}			
Sr_3UO_6	CF	0.0	0.64	2.18			
	FDMNES	0.0	0.6-0.69	1.8-2.03			

Table S2: Wybourne CF parameters for calculations shown in Figure 5.

sample	B_0^2 (eV)	B_0^4 (eV)	$B_4^4 = B_{-4}^4$ (eV)	B_0^6 (eV)	$B_4^6 = B_{-4}^6$ (eV)
$Cs_2UO_2Cl_4$	4.035	9.739	1.712	6.663	-2.041
$SrUO_4$	2.535	7.114	1.667	2.429	-1.520
Sr_3UO_6	-	4.425	-	0.716	-

Example of FDMNES input file:

```
Filout
out

Edge
M4

Range
-7.0 .1 -5.0 .005 0.0 .05 2.0 0.01 3.2 .1 7.0
Radius
6.0

SCF
N_self
100
P_self
0.05
E_cut
-4.5

Relativism
Spinorbit

Density_all
Harm_tess

COOP_atom
1
COOP_dist
2.7

Memory_save
```

```
Excited
Screening
0.6
```

Using space group:

```
Spgroup
C1m1

Crystal
 12.0058   7.6973   5.8503   90.  100.  90.

92     0.000000     0.0000000     0.000000
55     0.334440     0.0000000     0.678280
55     0.665040     0.0000000     0.323690
17     0.102320     0.2479300     0.794930
17     0.400020     0.2462200     0.206630
8      0.115240     0.0000000     0.236980
8      0.882230     0.0000000     0.768670
```

Using a cluster around U with rotated coordinates for projected DOS reflecting the local symmetry:

```
Absorber
1

Sym
1

Molecule
 1.00000   1.0000   1.0000   90.  90.  90.
92      0.0000000000      0.0000000000      0.0000000000
8       0.0171797648     -0.0171797648      1.7792080641
8       0.0171905644     -0.0171905644     -1.7803264856
17     -2.6644439697     -0.0344292559     -0.0415671431
17      0.0344292559      2.6644439697     -0.0415671431
17     -0.0763326660     -2.6862213612      0.0174638703
17      2.6862213612      0.0763326660      0.0174638703
55     -2.6861081123     -2.7567050457      2.4882967472
55      2.7567050457      2.6861081123      2.4882967472
…

Convolution
Gamma_hole
0.2
Gamma_max
0.5

End
```

References:

(1) Prieur, D. B.; Popa, K.; Vigier, J.-F.; Scheinost, A. C.; Martin, P. M. Crystallographic Structure and Charge Distribution of AUO4 and A3UO6 Uranates (A = Ca, Sr, Ba or Pb). *J. Nucl. Mater.* **2019**, *516*, 303–308.