On the calculation of multiplet energies of three-open-shell $4f^{13}5f^n6d^1$ electron configuration by LFDFT: modeling the optical spectra of $4f$ core-electron excitation in actinide compounds

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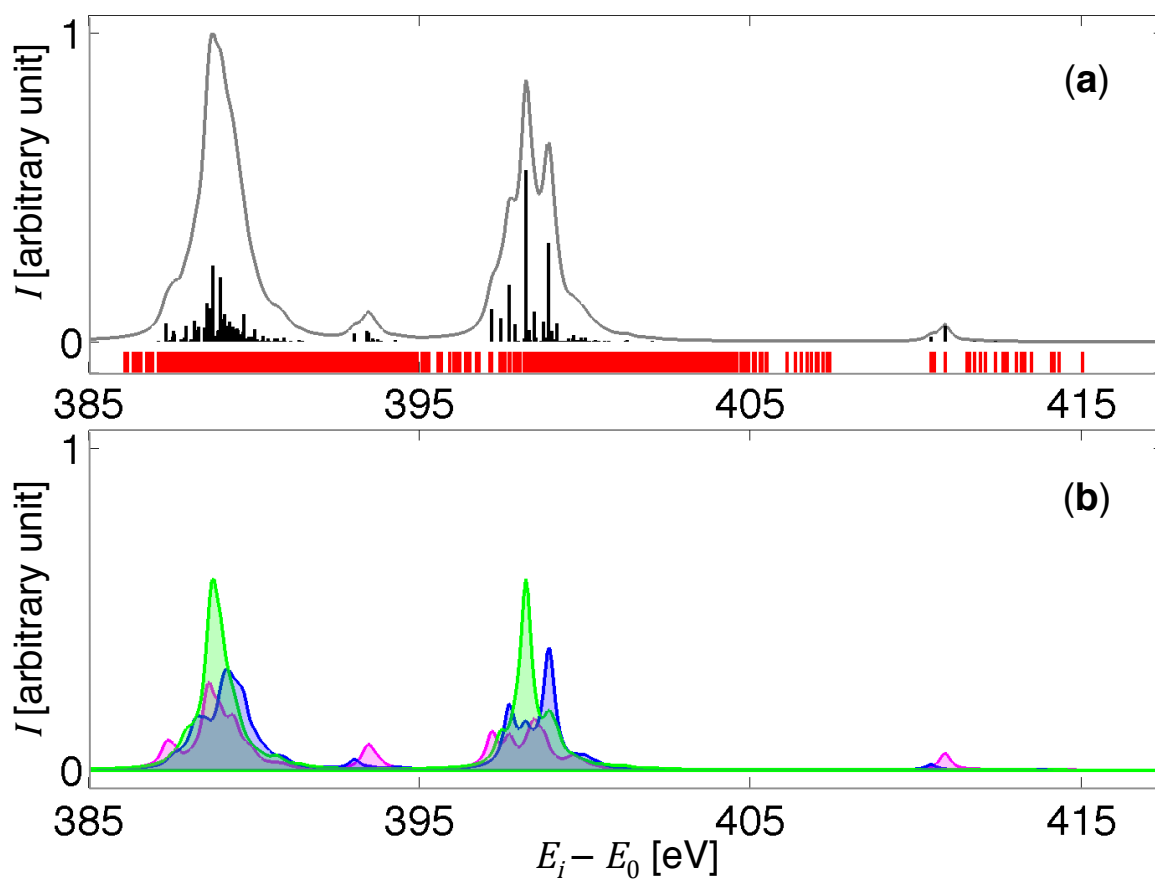**Electronic Supplementary Information ESI (6 pages)**

Fig. S1 LFDFT results of free U^{4+} ion obtained from DFT calculation using the LDA SVWN functional, showing the multiplet energies of the configuration $4f^{13}5f^26d^1$ (in red) and intensity of the $5f^2 \rightarrow 4f^{13}5f^26d^1$ transitions, *i.e.* oscillator strengths (in black) and Lorentzian broadening (in grey) (a) and the deconvolution of the intensity as function of final electronic states with $J = 3$ (in magenta), $J = 4$ (in blue) and $J = 5$ (in green) values (b). In the ordinates, the intensity plots are given in arbitrary unit.

Fig. S2 LFDFT results of free U^{4+} ion obtained from DFT calculation using the hybrid B3LYP functional, showing the multiplet energies of the configuration $4f^{13}5f^26d^1$ (in red) and intensity of the $5f^2 \rightarrow 4f^{13}5f^26d^1$ transitions, *i.e.* oscillator strengths (in black) and Lorentzian broadening (in grey) (a) and the deconvolution of the intensity as function of final electronic states with $J = 3$ (in magenta), $J = 4$ (in blue) and $J = 5$ (in green) values (b). In the ordinates, the intensity plots are given in arbitrary unit.
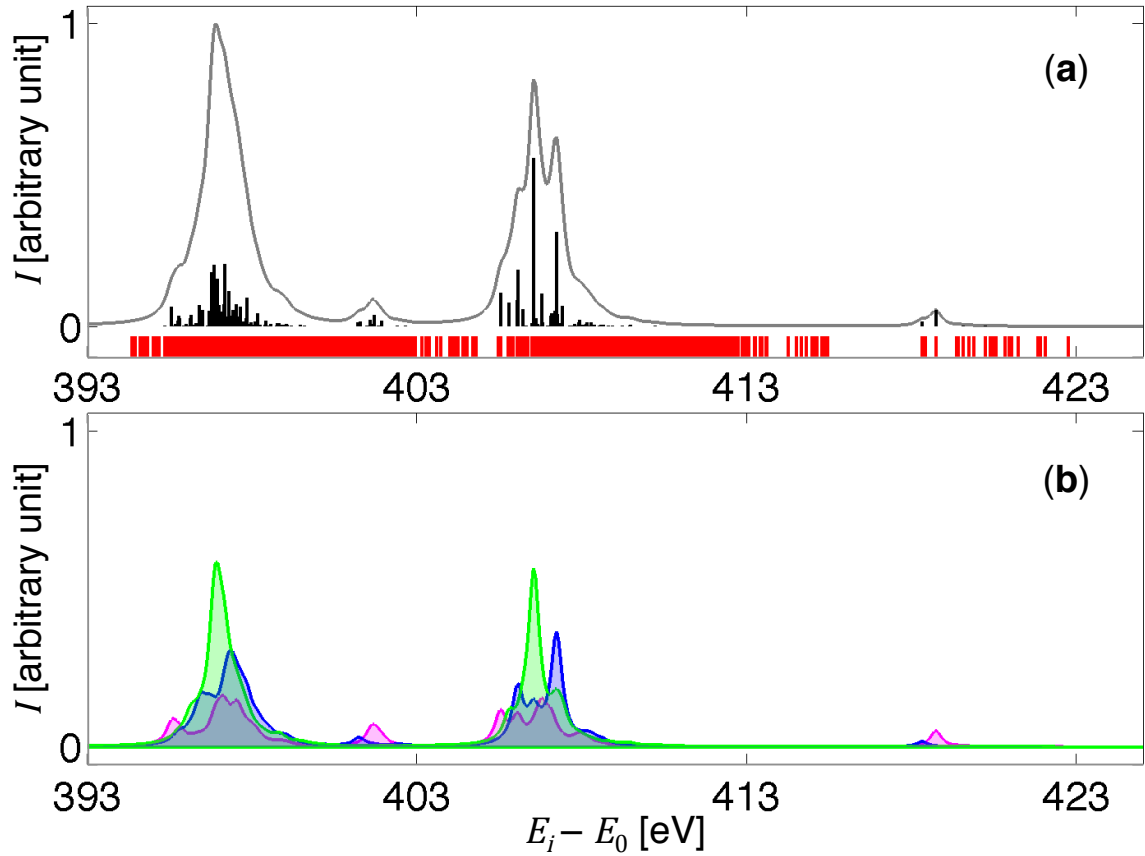
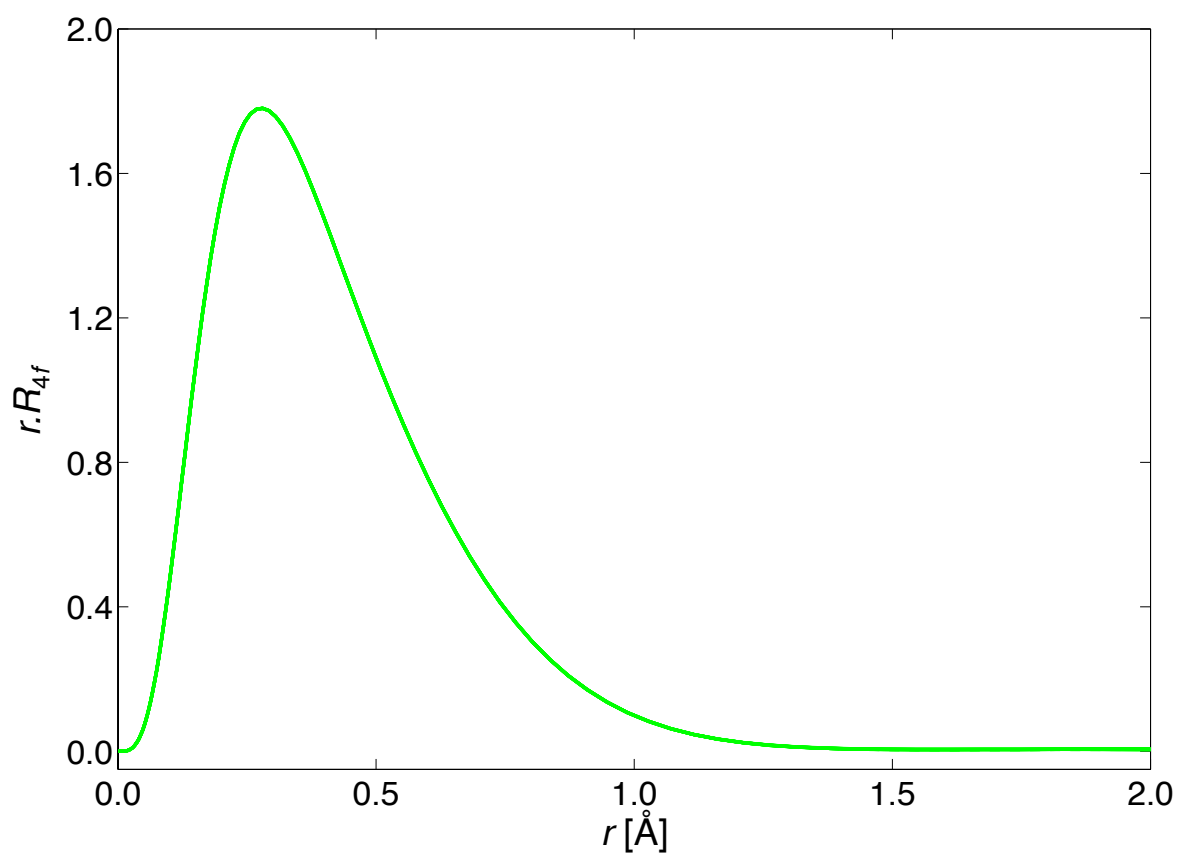**Fig. S3** Calculated radial functions of the Kohn-Sham orbitals with dominant uranium $4f$ (a) character obtained for the configuration $4f^{13}5f^26d^1$ in the free ion (dashed curve) and in $(UO_8)^{12-}$ (solid curve). They are needed for the evaluation of the Slater-Condon integrals (see the text for details). The changes of the radial functions from free ion to molecular cluster are highlighted.

Table S1. Calculated excitation energies ($E_i - E_0$), oscillator strengths (I) and assignment of the multiplet terms with non-zero transition probabilities obtained in the intra-atomic $5f^2 \rightarrow 4f^{13}5f^26d^1$ electron transitions in U^{4+}.

$E_i - E_0$	I	Assignment
		$\lvert 4f^{13}5f^26d^1, J = 5\rangle$
387.526	0.0032	15.79 % ^{5}H + 16.76 % ^{3}I + …
387.785	0.0014	11.77 % ^{5}G + 12.90 % ^{5}H + …
387.908	0.0014	
387.935	0.0102	10.84 % ^{1}H + …
388.075	0.0014	17.68 % ^{5}G + 10.19 % ^{5}H + …
388.237	0.0071	17.00 % ^{5}F + 12.44 % ^{3}G + …
388.538	0.0018	15.39 % ^{5}F + 12.49 % ^{3}G + …
388.614	0.0135	
388.657	0.0210	13.48 % ^{5}F + 13.05 ^{5}G % + …
388.730	0.0117	
388.750	0.0476	
388.787	0.0038	
388.931	0.0025	
388.976	0.0404	18.12 % ^{3}I + …
389.079	0.0012	15.40 % ^{5}G + …
389.180	0.0100	12.15 % ^{5}F + 11.05 % ^{3}I + …
389.294	0.0069	12.49 % ^{5}H + …
389.358	0.0094	
389.494	0.0074	11.73 % ^{3}H + …
389.549	0.0030	12.49 % ^{5}G + …
389.817	0.0030	10.36 % ^{3}G + …
390.015	0.0010	
390.087	0.0015	
390.238	0.0013	
390.619	0.0020	
390.687	0.0023	
397.424	0.0145	18.69 % ^{5}K + 28.54 % ^{5}I + …
397.868	0.0111	22.23 % ^{5}K + 16.13 % ^{5}K + 16.53 % ^{3}I + 16.32 % ^{3}I + …
398.196	0.1073	11.29 % ^{3}I + 27.78 % ^{5}K + 21.47 % ^{3}I + …
398.324	0.0012	10.13 % ^{3}G + 13.87 % ^{5}K + 10.46 % ^{1}H + 13.72 % ^{5}K + …
398.472	0.0026	10.31 % ^{5}I + 12.48 % ^{3}I + …
398.880	0.0156	16.19 % ^{5}I + …
398.893	0.0035	25.72 % ^{5}K + 11.49 % ^{3}I + …
398.953	0.0023	18.70 % ^{5}K + …
399.123	0.0115	14.81 % ^{5}I + 13.26 % ^{5}K + …
399.599	0.0023	13.69 % ^{5}I + …
401.242	0.0011	11.91 % ^{1}H + …
		$\lvert 4f^{13}5f^26d^1, J = 4\rangle$
387.585	0.0049	13.92 % ^{3}G + 19.49 % ^{5}G + 12.87 % ^{3}H + …
387.881	0.0026	12.45 % ^{5}H + …
388.096	0.0017	13.64 % ^{3}H + …
388.186	0.0129	17.54 % ^{3}H + …
388.308	0.0097	11.27 % ^{5}D + …
388.498	0.0089	15.67 % ^{3}H + …
388.555	0.0030	
388.632	0.0021	22.36 % ^{3}G + …
388.922	0.0023	
388.981	0.0144	14.49 % ^{3}F + …
389.104	0.0172	
389.157	0.0087	
389.257	0.0128	
389.288	0.0052	
389.402	0.0011	
389.429	0.0076	
389.469	0.0083	14.44 % ^{3}H + …
389.558	0.0048	11.71 % ^{3}F + …
389.658	0.0062	

389.678	0.0172	12.00 % ^{5}D + …
390.007	0.0080	
390.256	0.0035	
390.415	0.0021	12.23 % ^{3}H + …
390.893	0.0025	21.18 % ^{3}H + …
393.016	0.0054	11.82 % ^{5}I + …
397.691	0.0355	18.88 % ^{5}I + 20.58 % ^{3}H + 15.24 % ^{5}H + …
398.184	0.0182	12.15 % ^{5}I + 12.27 % ^{3}H + …
398.502	0.0029	10.26 % ^{5}F + 15.84 % ^{5}H + 13.39 % ^{3}G + …
398.780	0.0029	
398.886	0.0616	19.51 % ^{5}I + 11.49 % ^{5}I + 11.71 % ^{3}H + …
398.963	0.0068	18.92 % ^{5}I + …
399.003	0.0013	
399.742	0.0011	10.52 % ^{5}H + …
399.999	0.0027	11.67 % ^{5}I + …
410.425	0.0033	19.95 % ^{1}G + 69.66 % ^{3}H + …
	$|4f^{13}5f^26d^1, J = 3>$	
387.330	0.0114	12.65 % ^{5}H + 22.26 % ^{5}G + 22.56 % ^{5}G + 11.02 % ^{3}G + 15.69 % ^{3}G + …
387.445	0.0012	14.83 % ^{3}F + …
387.565	0.0069	17.29 % ^{5}F + 10.41 % ^{3}G + 12.53 % ^{3}F + …
387.928	0.0010	
388.190	0.0015	11.75 % ^{5}D + …
388.568	0.0242	17.60 % ^{3}G + …
388.613	0.0137	10.43 % ^{3}G + …
388.702	0.0073	
388.789	0.0015	18.84 % ^{3}F + …
388.884	0.0067	13.40 % ^{5}D + …
388.923	0.0073	
389.003	0.0079	10.77 % ^{3}G + …
389.075	0.0011	
389.153	0.0014	13.27 % ^{1}F + …
389.322	0.0065	
389.329	0.0074	
389.371	0.0035	
389.443	0.0055	
389.511	0.0012	11.86 % ^{3}D + …
389.639	0.0011	
389.724	0.0019	
389.777	0.0013	
389.907	0.0014	
389.924	0.0029	
390.014	0.0012	
390.881	0.0010	
393.381	0.0067	
393.451	0.0060	17.34 % ^{3}D + …
393.559	0.0020	18.36 % ^{3}F + 10.36 % ^{3}F + 11.90 % ^{1}F + …
393.605	0.0012	11.68 % ^{3}D + …
393.727	0.0018	
397.167	0.0205	19.92 % ^{5}H + 36.06 % ^{3}G + …
397.689	0.0166	14.57 % ^{5}H + 10.31 % ^{3}G + 11.39 % ^{3}G + …
398.150	0.0023	12.83 % ^{5}G + 12.04 % ^{3}F + …
398.305	0.0072	16.00 % ^{3}G + 10.84 % ^{1}F + 10.08 % ^{1}F + …
398.454	0.0191	10.42 % ^{3}F + 15.57 % ^{3}G + …
398.730	0.0126	
398.756	0.0015	
399.065	0.0014	
399.476	0.0019	10.70 % ^{5}H + …
399.640	0.0044	10.79 % ^{5}H + 13.74 % ^{5}G + …
399.871	0.0026	17.58 % ^{5}H + …
410.847	0.0102	69.75 % ^{3}G + 17.34 % ^{1}F + …