Electronic Supplementary Information (ESI)

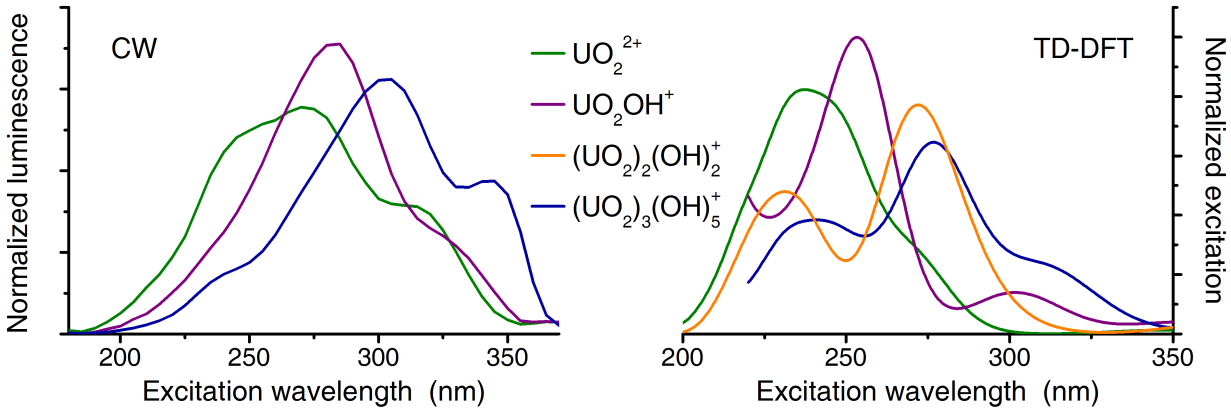

Figure S1: Comparison of experimental revealed and calculated (TD-DFT) excitation spectra. Assignment of the 1:1 complex is supported by relative peak positions and spectra shape.

TD-DFT

TD-DFT is not necessarily the best method to study the excited states of uranyl(VI). It is well-known that a multireference method gives more accurate energy levels but only with large computational cost. This has been tested on triatomic uranyl(VI) ion.[1] Only a few excited states can be calculated for the hydrated uranyl(VI) ion. For example, previous authors utilized CAS-SCF(12/11)[2] or CASPT2(12/12)[3] to calculate uranyl complexes. These methods are based on an active space of 12 electrons in 11 or 12 orbitals, respectively. In both cases the authors could only consider less than 10 excited levels. In the present TD-DFT calculations, we included 100 to 200 excited levels (only singlet states) which was mandatory to reach the water-to-uranium LMCT states. From a technical point of view TD-DFT is currently the only method for calculations of excitation spectra of uranyl(VI) hydrate as obtained here. Furthermore in the water-to-uranium LMCT states multireference character of the system becomes relatively less important (compared to O_{yl}-to-uranium LMCT states) thereby justifying the use of TD-DFT. We nevertheless admit exploratory character of the present computations.

References

[1] F. Réal, V. Vallet, C. Marian and U. Wahlgren, *J. Chem. Phys*, 2007, **127**, 214302.

[2] F. P. Rotzinger, *Chem. Eur. J.*, 2007, **13**, 800–811.

[3] L. Gagliardi, *Int. J. Quantum Chem.*, 2011, **111**, 3302–3306.

Table S1: Atomic coordinates for the uranyl(VI) aquo ion

U	0.000569	-0.019281	0.00025
O	-0.001001	-0.051361	-1.749018
O	-0.016094	2.439981	0.0022
O	0.004567	-0.056549	1.749477
O	2.337055	0.822881	-0.009381
O	1.574971	-1.883907	-0.003007
O	-1.558724	-1.897887	0.001094
O	-2.345703	0.797843	0.005941
H	-0.018049	3.007829	-0.780381
H	-0.022077	3.005565	0.786388
H	2.610428	1.747444	0.02718
H	3.122334	0.262914	0.022528
H	1.844138	-2.380643	-0.787234
H	1.84247	-2.38632	0.778177
H	-1.819928	-2.402308	-0.780912
H	-1.81988	-2.400245	0.784422
H	-3.126375	0.231267	-0.022986
H	-2.625978	1.720354	-0.028649

Table S2: Atomic coordinates for the uranyl(VI) 1:1 hydroxo complex

U	0.006392	-0.09521	0.005211
O	-0.028676	-0.015282	1.777452
O	-2.413076	-0.790928	0.001828
O	0.007249	-0.064283	-1.767178
O	0.361121	-2.195753	0.049096
O	2.52665	-0.317562	0.084254
O	1.141667	2.163467	-0.046145
O	-1.648887	1.858802	-0.06209
H	-2.786696	-1.306093	0.727901
H	-2.854677	-1.07145	-0.809751
H	0.455487	-2.807276	-0.690492
H	2.897074	-1.207502	0.043039
H	3.161944	0.296368	-0.302774
H	1.550915	2.604323	0.708952
H	1.369381	2.664565	-0.839375
H	-1.386801	2.756979	0.171332
H	-2.563093	1.721748	0.213989

Table S3: Atomic coordinates for the uranyl(VI) 2:2 hydroxo complex

U	-1.943542	-0.028528	0.000489
U	1.943557	-0.028546	0.000539
O	-2.012094	-0.089233	-1.762589
O	-2.590226	2.411696	-0.073196
O	-2.01968	-0.007479	1.763764
O	-4.429642	0.321566	0.091771
O	-2.842721	-2.335885	-0.015329
O	-0.000005	-1.324393	-0.005071
O	-0.000022	1.29081	0.070114
O	2.012134	-0.089205	-1.762544
O	2.019787	-0.007407	1.763809
O	2.843232	-2.335639	-0.015159
O	4.429421	0.321837	0.091882
O	2.589688	2.411767	-0.072932
H	-2.132944	3.067171	-0.614039
H	-3.52691	2.643974	-0.042556
H	-5.023364	0.229026	-0.664422
H	-4.950702	0.183939	0.892979
H	-3.157625	-2.810671	-0.794497
H	-3.019723	-2.881748	0.760904
H	3.15802	-2.810461	-0.794351
H	3.020192	-2.881525	0.761066
H	5.023339	0.229516	-0.664177
H	4.950455	0.185209	0.893275
H	2.132553	3.066889	-0.61433
H	3.526311	2.644252	-0.041957
H	-0.000109	-2.145826	-0.512073
H	0.0001	1.983576	0.743361

Table S4: Atomic coordinates for the uranyl(VI) 3:5 hydroxo complex

U	-0.735791	2.093308	0.012658
U	-1.442545	-1.685621	0.012669
U	2.18037	-0.408397	0.011849
O	0.001478	0.000517	0.107081
O	-0.800879	2.242913	1.790458
O	-0.753454	2.178299	-1.769864
O	-1.552289	-1.804493	1.790561
O	-1.491439	-1.756379	-1.770003
O	2.347557	-0.44065	1.788804
O	2.258522	-0.417108	-1.771153
O	-2.480016	0.464219	0.016894
O	0.838593	-2.383673	0.036558
O	1.645864	1.920386	0.037332
O	0.068936	4.503106	-0.036463
O	-2.87173	3.461375	-0.097068
O	-3.929751	-2.187893	-0.0694
O	-1.571444	-4.223434	-0.050443
O	3.858537	-2.313553	-0.088104
O	4.442616	0.738238	-0.066907
H	-3.320155	0.618947	-0.427294
H	1.127665	-3.197552	-0.388985
H	2.201828	2.57559	-0.397051
H	0.24217	5.047206	0.74072
H	0.082432	5.079519	-0.80965
H	-3.435295	3.694044	0.65006
H	-3.305511	3.766051	-0.902535
H	-4.53111	-2.20411	0.684366
H	-4.450552	-2.333382	-0.867795
H	-1.627888	-4.802927	0.718352
H	-1.726686	-4.758588	-0.837405
H	4.259572	-2.744669	0.675605
H	4.348465	-2.586569	-0.872559
H	4.923479	1.090158	0.691197
H	4.935687	0.966585	-0.86349