Supplementary Information for The Role of Cations in Uranyl Nanocluster Association: A Molecular Dynamics Study

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Uranyl Peroxide Subunit Simulations

Atomic charges for the uranyl peroxide unit can be found in Table S1 and were derived from CM5 calculations. Due to rounding error, the charges do not exactly sum to zero. GROMACS handles this by applying a uniform background charge. The LJ parameters were the same as those used for the simulation of the nanocluster. In addition, all MD simulation protocol details were kept the same. Non-bonded interactions were excluded for atoms connected by at most 3 bonds. One uranyl peroxide ion was simulated with 1000 SPC/E water molecules. The peroxide species was kept approximately rigid through use of a very stiff bond stretching, angle bending and dihedral potentials.

Table S1: Charges used in uranyl peroxide simulations, derived from CM5 calculations.

Atom type	$[(UO_2)_2O_2]^{2+}$
U	2.902655
Ou	-0.732414
Op	-0.437646

Tables S2-S7 show the QM single point energy data used to fit the LJ parameters for both the peroxide and the nanocluster. The configurations refer to those found in Figure 3 in the main text.

Table S2: QM Energy Calculations: Configuration A

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.0	75.4330	61.3519
1.5	11.9070	6.4712
2.0	3.6989	1.2547
2.2	3.2340	1.3776
2.4	3.1574	1.7101
2.6	3.2142	2.0557
2.8	3.2925	2.3417
3.0	3.3512	2.5538
3.5	3.3451	2.7926
4.0	3.1847	2.7722
4.5	2.9506	2.6254
5.0	2.6981	2.4348
6.0	2.2237	2.0364
7.0	1.8319	1.6911
10.0	1.0842	1.0101

Table S3: QM Energy Calculations: Configuration B

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.0	428.3077	359.3745
1.5	102.5708	76.1614
2.0	4.0634	-3.9124
2.2	-6.5949	-11.4957
2.4	-11.3355	-14.3022
2.6	-13.1380	-14.8704
2.8	-13.5210	-14.4526
3.0	-13.2334	-13.6467
3.5	-11.6005	-11.3508
4.0	-9.8819	-9.4469
4.5	-8.4185	-7.9451
5.0	-7.2172	-6.7619
6.0	-5.4279	-5.0585
7.0	-4.2056	-3.9118
10.0	-2.2500	-2.0900

Table S4: QM Energy Calculations: Configuration C

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.0	90.7210	78.1486
1.5	18.9529	10.6208
2.0	6.2668	1.7233
2.2	4.8338	1.2922
2.4	4.0725	1.3078
2.6	3.6445	1.4862
2.8	3.3849	1.6973
3.0	3.2061	1.8832
3.5	2.9057	2.1744
4.0	2.6691	2.2543
4.5	2.4509	2.2147
5.0	2.2487	2.0926
6.0	1.8916	1.8123
7.0	1.5947	1.5437
10.0	0.9943	0.9588

Table S5: QM Energy Calculations: Configuration D

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.0	102.2088	85.9486
1.5	24.2574	15.0047
2.0	8.1254	3.1877
2.2	6.1512	2.3362
2.6	4.4062	2.1367
2.8	4.0081	2.2559
3.0	3.7389	2.3818
3.5	3.3078	2.5861
4.0	3.0051	2.6086
4.5	2.7427	2.5134
5.0	2.5017	2.3590
6.0	2.0855	1.9823
7.0	1.7459	1.6847
10.0	1.0698	1.0341

Table S6: QM Energy Calculations: Configuration E

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.0	79.7692	69.4484
1.5	14.2823	8.8026
2.0	4.6500	1.9744
2.2	3.8878	1.8621
2.4	3.6105	2.0412
2.6	3.5309	2.3054
2.8	3.5140	2.5434
3.0	3.5026	2.7350
3.5	3.4026	2.9490
4.0	3.2031	2.9081
4.5	2.9579	2.7525
5.0	2.7063	2.5583
6.0	2.2426	2.1425
7.0	1.8587	1.7808
10.0	1.1152	1.0677

Table S7: QM Energy Calculations: Configuration F

Distance (Å)	HF Energy (kJ/mol)	MP2 Energy (kJ/mol)
1.8	-	166.685
2.0	-	-73.471
2.2	-	-167.338
2.25	-	-177.675
2.3	-	-184.507
2.35	-	-188.477
2.4	-	-190.137
2.5	-	-188.274
2.7	-	-172.518
3.0	-	-139.816
3.3	-	-110.097
3.6	-	-86.9871
4.0	-	-65.2606
5.0	-	-37.1026

RDF plots along with cumulative RDF plots of U-Ow (oxygen of water) interactions for uranyl peroxide are shown in Fig. S1. The peak of the RDF for uranyl peroxide is at 0.250 nm. Cumulative RDF plots suggest that the uranyl peroxide has four water molecules per uranium atom in their first solvation shell. A more detailed picture of solvation can be seen in the SDF plots, shown in Fig. S2. It can be seen that the U atom of uranyl peroxide is hexa-coordinated (two peroxide oxygen atoms plus four water oxygen atoms). In uranyl peroxide, the two peroxide oxygen atoms present in the vicinity of U repel the water molecules, which increases the radius of the solvation shell and allows a hexa-coordinated configuration. The results of uranyl peroxide agree well with the simulation results by Mir et al.[1] and experiments.[2,3]

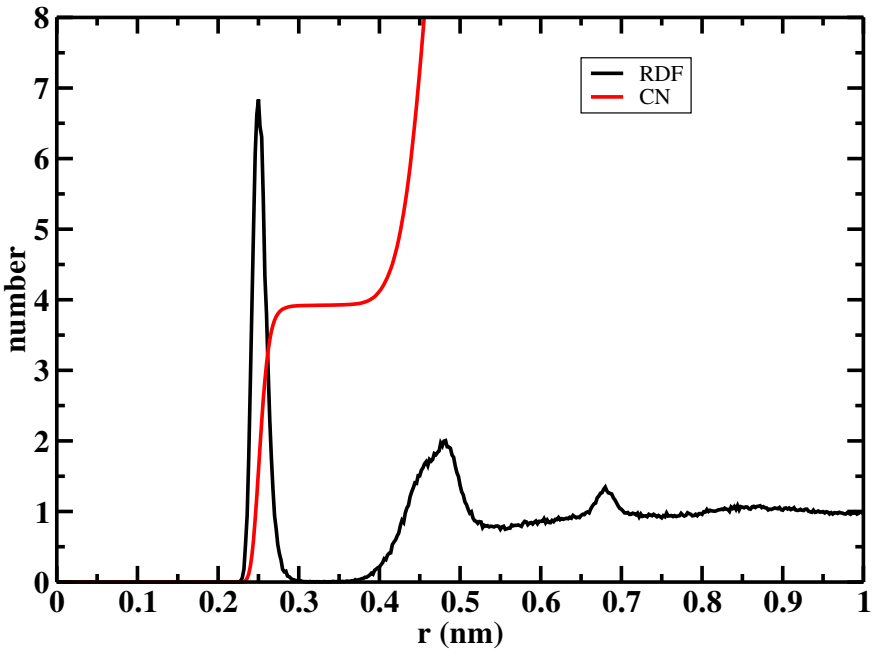
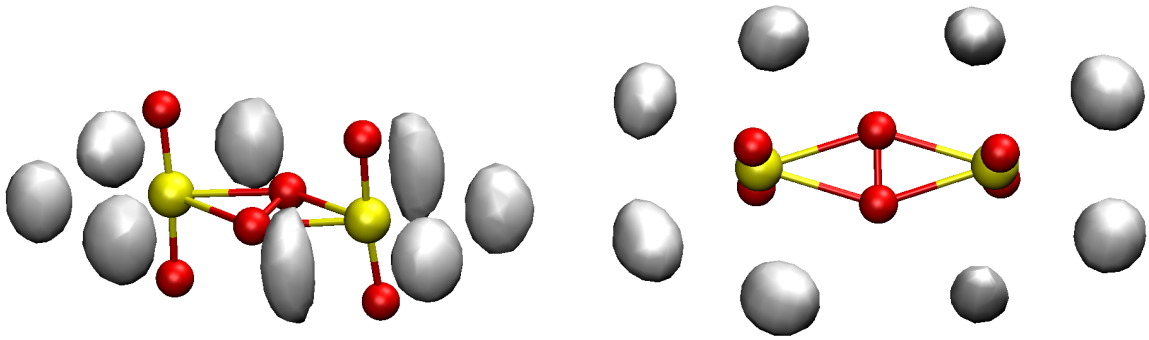


Figure S1: Radial distribution function (RDF) and cumulative RDF (CN) between U and Ow atoms for $[(UO_2)_2O_2]^{2+}$ ion in water.



(a) (b)

Figure S2: Spatial distribution function (SDF) of water molecules around $[(UO_2)_2O_2]^{2+}$. (a) Front view, (b) Top view.

REMD Simulations

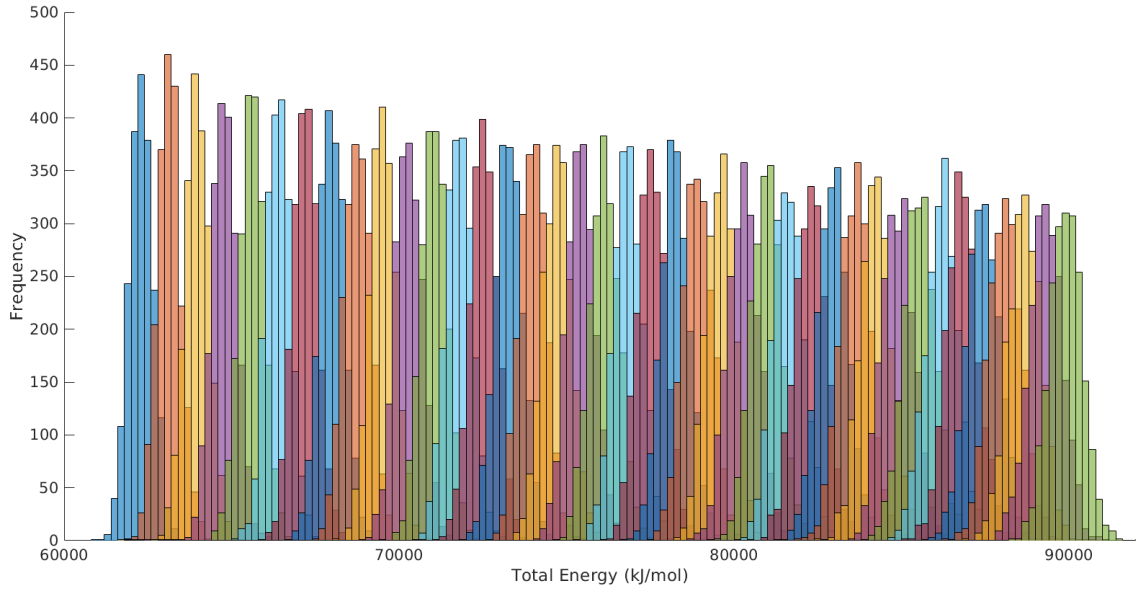


Figure S3: Energy histograms for REMD simulations. Simulations range from 298K to 500K, in increasing order from left to right.

References

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(2) Burns, P. C. U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. *Can. Mineral.* **2005**, *43*, 1839–1894.

(3) Sigmon, G. E.; Ling, J.; Unruh, D. K.; Moore-Shay, L.; Ward, M.; Weaver, B.; Burns, P. C. Uranyl-Peroxide Interactions Favor Nanocluster Self-Assembly. *J. Am. Chem. Soc.* **2009**, *131*, 16648–16649.