

Hydration of the sulfate dianion in cold nanodroplets :



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Supplementary information

Section S-1 provides informations on the efficiency of the exploration procedure.

Section S-2 completes the description and analysis of the computed spectra for $n=13$, with the cases of W13-5 and W13-7.

Tables S1 and S2 include relative energies of the several most stable isomers of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$ and $\text{SO}_4^{2-}(\text{H}_2\text{O})_{13}$, computed at all levels mentioned in section 2.

Tables S3 and S4 provide the cartesian coordinates of the optimized structures of the single most stable isomers of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$ and $\text{SO}_4^{2-}(\text{H}_2\text{O})_{13}$, computed at the M11/6-311++G(d,p) level.

S-1. Efficiency of the exploration procedure

The selected snapshots from MD trajectories were used without local geometry optimization before switching to DFT. Such structures often involve one or several water molecules that are only loosely bound to the cluster, e. g. by only one hydrogen bond. DFT geometry optimization creates these “missing” hydrogen bonds, thus yielding more compact structures, however without significant restructuring of the cluster. This indicates that the AMOEBA force field is able to capture the main energy components of both ion-water and water-water interactions, and that the temperature of 200 K is in the appropriate range. Too high a temperature would generate higher energy structures, leading to extensive structural reorganization during DFT optimization. Too low a temperature, or too small a time step, would often generate identical structures in successive steps, which was nearly never observed. In ca. 10% of the cases, the final DFT energy was more than 30 kJ.mol⁻¹ higher than that of the most stable structure. When one or several water molecules are loosely bound and oriented in an unfavorable manner to establish one more hydrogen bond, the optimization procedure leads to trapping into a local minimum, however high in energy. Overall, the procedure used appears to be appropriate to generate a broad exploration of the low energy portions of the potential energy surface, although it cannot be claimed that *all* low energy structures, nor even *the* lowest energy structure, have been identified for each cluster size.

A number of isomers of SO₄²⁻(H₂O)₁₃ were found to be similar in the sense that their oxygen network and connectivity are identical and they differ only by the partial reversal of the hydrogen bonds. Another type of similarity is when the 13th water molecule is added to one of several sites of a single SO₄²⁻(H₂O)₁₂ core. A particularly clear case is that of W12-1. To this structure, the 13th water can be added either to a “vertical” or a “horizontal” edge of one of the (H₂O)₄ clusters (in the orientation shown in Figure 3, see W13-1d and W13-1c), or bridging between two such clusters (W13-1a), or bridging between one cluster and a sulfate oxygen (W13-1e), or bridging between two sulfate oxygens (W13-1b). This W13-1 structural family is found to span an energy range of at least 6.5 kJ.mol⁻¹ (see Table 2).

Each of these five options was indeed found at least once by the search procedure used, a very encouraging result. On the other hand each of the five can also be combined to several

different H-bonding network orientations, as discussed above for $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$. Out of these numerous options, only 9 were found by the present search (spanning a $6.5 \text{ kJ}\cdot\text{mol}^{-1}$ energy window); each and every one of the four independent MD runs contributed to finding these 9 combinations. This underlines the efficiency of using several different starting points in the MD procedure, but also the fact that the present conditions cannot be claimed to be sufficient to identify *all* low energy structures. Reversal of H-bonding orientation within one water tetramer requires simultaneous exchange of four hydrogen bonds. Although energetically accessible, this turned out to be a rare process for both $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$ and $\text{SO}_4^{2-}(\text{H}_2\text{O})_{13}$ in the MD conditions used here. Taking this effect into full account would require a specific treatment of ring inversion.^{S1}

Reference S1 : A. A. Hagberg, D. A. Schult, P. J. Swart, Exploring network structure, dynamics, and function using NetworkX. Proceedings of the 7th Python in Science Conference (SciPy2008). Pasadena, CA USA, 2008; pp 11–15

S-2. Description of additional spectra : W13-5 and W13-7

The spectrum of W13-5 is somewhat different and thus deserves additional details. The structure consists in three rings, each comprising 3 water molecules and one sulfate O, with each water donating one H bond to the sulfate, plus a cyclic $(\text{H}_2\text{O})_4$ donating two H bonds to water molecules and two to the sulfate top of W13-5 in Figure 4). It is the most saturated sulfate structure in the low energy manifold. The higher saturation of the sulfate leads to only one sulfate stretching band near 1150 cm^{-1} instead of two for most other structures, and two nearly degenerate components at 1067 and 1070 cm^{-1} . A weaker band at 1038 cm^{-1} (appearing as a shoulder in Figure 4), absent in other spectra, arises from water libration in the $(\text{H}_2\text{O})_4$ cluster. A relatively intense band at 970 and a smaller one at 936 cm^{-1} appear in a region with less activity in other spectra. They arise from motions of water molecules in the vicinity of the $(\text{H}_2\text{O})_4$ cluster. Starting with the next intense band at 936 cm^{-1} is the more common delocalized water libration massif. While this spectrum could easily account for the experimental band at 970 cm^{-1} , it is in less good agreement for the sulfate stretching frequencies.

W13-7 is an example of a structure with a water molecule bridging between two sulfate O's, with distances of 1.97 and 2.02 Å, ca. 0.15 Å longer than for tightly bound first shell molecules. Thus the sulfate oxygen coordination is denoted as [3,"3","3",2] in Table 2. The single 2-coordinated S-O bond generates a single stretching band at 1140 cm⁻¹ and two close ones at 1069 and 1082 cm⁻¹, leading to a different pattern in this region. A libration band appears at 994 cm⁻¹, delocalized however with no component on the weakly bound H₂O.

Isomer name	M11/basis1 ^a no ZPE	M11/ basis1 ^a	M11/ basis3 ^c	MP2/ basis2 ^b	CC2/ basis2 ^b	MP2 /basis3 ^c	CC2 /basis3 ^c	DLPNO- CCSD(T) /basis2 ^b	DLPNO- CCSD(T) /basis3 ^c
W12-1a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W12-1b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W12-1c	0.4	0.0	1.4	2.2	2.3	2.4	2.5	2.2	2.1
W12-1d	1.7	1.4	5.1	5.8	6.0	6.3	6.5	7.0	6.2
W12-2	9.3	3.7	4.5	12.6	14.0	15.6	17.0	13.6	8.2
W12-3	9.1	4.0	5.2	13.4	15.2	16.7	18.3	11.5	8.5
W12-4	10.5	7.7	8.0	9.8	10.3	10.2	10.8	10.5	8.9
W12-5	13.2	8.0	5.3	14.6	16.3	19.0	20.6	10.7	10.0
W12-6	11.8	7.7	6.8	13.6	14.8	15.8	16.9	10.3	10.2
W12-7	4.9	4.0	7.3	11.9	12.2	12.1	12.3	11.4	10.8
W12-8	7.0	2.3	5.1	19.3	21.1	21.0	22.4	17.7	12.9
W12-9	11.2	8.3	9.3	17.5	18.7	20.9	21.9	16.1	13.1
W12-10	7.5	7.7	10.9	16.5	17.8	18.2	19.2	13.8	13.3
W12-11	12.1	6.1	6.6	22.8	24.4	25.4	26.7	23.4	17.7
W12-GL	24.3	16.4	14.6	24.5	26.7	24.4	26.2	21.7	19.0
W12-AN	43.5	33.9	21.7	30.5	32.2	35.8	37.9	30.0	27.0

Table S1. Relative energies (in $\text{kJ}\cdot\text{mol}^{-1}$) of the lowest energy isomers of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$. Names in boldface correspond to structures displayed in Figure 1, with spectra in Figure 2. ^aBasis 1 stands for 6-311++G(d,p). ^bBasis 2 stands for TZVPP. ^cBasis 3 stands for aug-cc-pVTZ. All geometries were optimized at the M11/6-311++G(d,p) level, and all relative energies were corrected for M11-computed 0 K vibrational energies.

Isomer name	M11/basis1 ^a no ZPE	M11/ basis1 ^a	M11/ basis3 ^c	MP2/ basis2 ^b	CC2/ basis2 ^b	MP2 /basis3 ^c	CC2 /basis3 ^c	DLPNO- CCSD(T) /basis2 ^b	DLPNO- CCSD(T) /basis3 ^c
W13-1a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W13-2	-0.2	0.6	6.3	3.3	4.2	4.7	5.4	3.1	1.2
W13-3	-1.6	0.8	1.3	2.0	1.2	2.4	1.8	2.1	2.9
W13-4	4.1	4.6	3.3	4.1	4.3	4.9	5.1	5.2	3.1
W13-1b	3.5	1.5	4.0	4.0	4.3	5.3	5.6	5.0	3.1
W13-1c	4.2	2.8	3.9	3.8	4.0	6.2	6.3	2.7	3.1
W13-5	-4.2	-4.1	2.0	5.3	5.8	8.2	8.7	7.7	3.2
W13-1b2	4.6	2.8	5.6	4.0	4.3	5.8	6.1	4.9	3.5
W13-6	1.7	1.4	2.2	5.5	6.3	8.9	9.7	6.1	3.6
W13-2b	3.7	4.6	5.5	6.2	6.2	7.9	7.8	4.2	4.0
W13-1b3	3.9	1.3	5.3	4.5	4.8	6.3	6.6	5.0	4.3
W13-1b4	3.3	2.5	5.3	5.0	5.2	6.3	6.6	6.0	4.4
W13-1d	3.4	4.0	5.9	7.2	7.4	9.1	9.2	6.5	5.1
W13-7	3.0	2.6	4.7	8.3	9.0	11.0	11.7	7.7	5.3
W13-8	3.8	3.0	0.9	6.7	6.9	5.9	6.2	6.8	5.7
W13-9	6.8	4.2	6.4	10.0	11.2	15.7	16.9	9.0	6.1
W13-1d2	3.2	4.4	7.1	7.7	7.9	10.1	10.3	6.5	6.3
W13-10	6.7	3.3	5.2	9.6	10.8	15.1	16.2	9.4	6.3
W13-1e	5.1	4.4	7.6	7.4	7.7	8.1	8.4	8.5	6.5
W13-11	4.2	5.3	8.9	10.3	10.8	13.0	13.5	9.3	8.3
W13-12	4.7	4.3	8.2	9.3	9.2	10.7	10.7	11.1	9.9
W13-13	4.4	5.1	7.8	9.4	9.3	10.5	10.5	12.4	9.9
W13-AN	28.7	23.0	15.9	23.7	23.6	41.8	35.3	22.2	19.5

Table S2. Relative energies (in $\text{kJ}\cdot\text{mol}^{-1}$) of the lowest energy isomers of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{13}$. Names in boldface correspond to structures displayed in Figure 3, with spectra in Figure 4. ^aBasis 1 stands for 6-311++G(d,p). ^bBasis 2 stands for TZVPP. ^cBasis 3 stands for aug-cc-pVTZ. All geometries were optimized at the M11/6-311++G(d,p) level, and all relative energies were corrected for M11-computed 0 K vibrational energies.

Atom	x	y	z
S	0.003059	-0.001084	-1.286586
O	0.649174	-1.272737	-1.737783
O	-1.420706	0.075832	-1.739805
O	0.001961	-0.000908	0.254182
O	0.781841	1.193768	-1.738591
O	3.389705	1.148871	-0.643039
H	3.261308	1.328401	0.30638
H	2.517273	1.273752	-1.062536
O	3.339643	-1.639287	-0.901124
H	2.468738	-1.651457	-1.338235
H	3.556437	-0.686401	-0.867836
O	-2.554695	1.744509	2.140909
H	-1.62319	2.026997	2.14092
H	-2.539737	0.771743	2.088241
O	-0.245908	3.707236	-0.904807
H	0.19983	2.958093	-1.340897
H	-1.18016	3.420355	-0.872859
O	0.19426	2.382322	1.530673
H	0.128301	1.536854	1.031527
H	0.137272	3.06063	0.828372
O	-2.686491	2.359092	-0.648728
H	-2.357196	1.540528	-1.066063
H	-2.780742	2.159797	0.30064
O	2.78126	1.33527	2.144177
H	1.93198	1.80951	2.091303
H	2.561008	0.387139	2.143778
O	-0.237923	-3.079573	2.142415
H	-0.946265	-2.412123	2.140905
H	0.598859	-2.583597	2.089944
O	-0.704501	-3.504847	-0.646993
H	-0.158687	-2.812099	-1.065119
H	-0.484025	-3.486076	0.30226
O	-2.162128	-1.016853	1.52654
H	-2.722863	-1.407155	0.826983
H	-1.397305	-0.653425	1.02481
O	1.965285	-1.365281	1.530993
H	1.267304	-0.883383	1.031989
H	2.583813	-1.651403	0.829558
O	-3.093968	-2.066275	-0.904798
H	-2.37813	-2.731477	-0.870548
H	-2.667254	-1.306985	-1.341926

Table S3. Cartesian coordinates of the optimized geometry of the lowest energy isomer of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{12}$, at the M11/6-311++G(d,p) level.

Atom	x	y	z
O	2.1463390975	-0.3589357139	3.301704255
O	3.3943016944	5.8956958242	0.7389968443
O	1.4298618475	4.4151951657	-0.6204722178
O	4.4602374429	3.2522811197	0.7968862746
S	.5671827896	2.4009160467	1.6388524115
O	2.1830718218	2.363450654	0.9686757884
O	4.0687050435	0.9965850679	1.7387148969
O	3.386322988	3.0004466783	3.0012813838
O	1.8988713964	2.4152261257	-2.614217616
O	-0.4915025303	4.672579458	1.4829521847
O	4.4168670372	-0.4060182171	-0.6996038477
O	1.1013176862	4.8117240256	5.8774285098
O	-0.130299261	2.0130040834	2.3312230597
O	0.0312006219	-0.6557965473	1.4786724044
O	4.6247340553	2.1546266603	-1.8182160893
O	1.7749066323	5.2798087849	3.0566786277
O	1.6829690206	0.248151191	-0.6980882744
H	2.8923254834	0.0132077675	2.7922236664
H	1.9127615542	0.3192538777	3.9553746736
H	2.9078824534	5.9092168838	1.5820426892
H	3.9355387113	5.0852719962	0.7745470637
H	3.7393953426	2.3189639204	-2.192299929
H	4.6481147172	2.6288944636	-0.9664408004
H	-0.3745174711	1.1006038624	2.0828405752
H	0.7363387431	2.1361154264	1.8814451069
H	1.6373516963	3.1911714626	-2.0886756536
H	1.6550473024	1.6336689076	-2.0879705452
H	0.762952127	-0.697791211	2.1267773537
H	0.4713731649	-0.5158690098	0.6221734587
H	0.9440555379	5.0880743072	2.5761024838
H	2.3072622127	4.4596463324	3.0578779244
H	2.5482131716	-0.195207395	-0.8067794883
H	1.876692513	0.9763422617	-0.0693520979
H	1.3060984953	5.1915410842	5.0081579376
H	1.1306516895	3.856855384	5.7126898174
H	-0.0139300154	4.639178427	0.6350521351
H	-0.6399576258	3.7478473782	1.7459883471
H	2.0576834539	5.1292394643	-0.399319438
H	1.7422348353	3.6745800691	-0.052170216
H	4.4392831577	-0.0757794052	0.2164143983
H	4.6241718639	0.3928088552	-1.2239502861
H	2.1864277252	2.4225614184	4.2276202969
O	1.395749599	2.1139825781	4.7136823177
H	0.6872961778	2.1301104859	4.0432406134

Table S4. Cartesian coordinates of the optimized geometry of the lowest energy isomer of $\text{SO}_4^{2-}(\text{H}_2\text{O})_{13}$, at the M11/6-311++G(d,p) level.