Manifolds of low energy structures for a magic number of hydrated sulfate : $SO_4^{2-}(H_2O)_{24}$ †

Electronic Supplementary Information

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Calibration of density functionals

Final calibration calculations were carried out at the DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/cc-pVTZ level for 9 low-energy structures of $SO_4^{2-}(H_2O)_{24}$. Such calculations were found to be too involved to be carried out more extensively. The cc-pVTZ basis was used instead in further DLPNO calculations. A calibration study for the 9 structures mentioned above can be found in Table S1, in which all relative energies are corrected for zero-point energies computed at the geometry optimization level. It can also be seen that relative energies differ at most by 1.8 kJ.mol^{-1} between ωB97X-D/aug-cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ. Thus ωB97X-D/aug-cc-pVTZ was deemed sufficiently accurate and kept for all final energy calculations. The better performance of M11 for small clusters in which sulfate-water interactions are dominant is less important in the present size range where all isomers have relatively similar interactions between sulfate and first-shell water molecules and it is the water network which is more discriminant.

Table S1 Calibration study on 0 K energetics of selected structures of $SO_4^{2-}(H_2O)_{24}$. M11, ωB97X-D and CCSD(T) values are computed at the M11/cc-pVTZ, ωB97X-D/cc-pVTZ and ωB97X-D/cc-pVTZ optimized geometries, respectively. All relative energies (in kJ.mol^{-1}) are corrected for zero-point energies computed at the geometry optimization level.

Structure name	M11 cc-pVTZ	M11 aug-cc-pVTZ	ωB97X-D cc-pVTZ	ωB97X-D aug-cc-pVTZ	CCSD(T) cc-pVTZ	CCSD(T) aug-cc-pVTZ
W24-A	0.0	0.0	0.0	0.0	0.0	0.0
W24-B	-15.1	-9.6	-0.9	1.8	0.6	3.6
W24-C	-9.2	-5.9	0.7	2.5	2.2	4.0
W24-D	-10.6	-6.1	2.6	4.0	2.1	3.8
W24-E	-8.8	-4.7	2.1	4.2	2.8	4.3
W24-F	-5.1	-4.0	3.2	4.4	3.2	3.7
W24-G	-11.4	-6.8	6.6	7.7	8.5	10.9
W24-H	-13.1	-7.3	6.0	9.7	7.1	9.4
W24-I	-10.5	-4.1	10.1	12.3	13.3	15.0

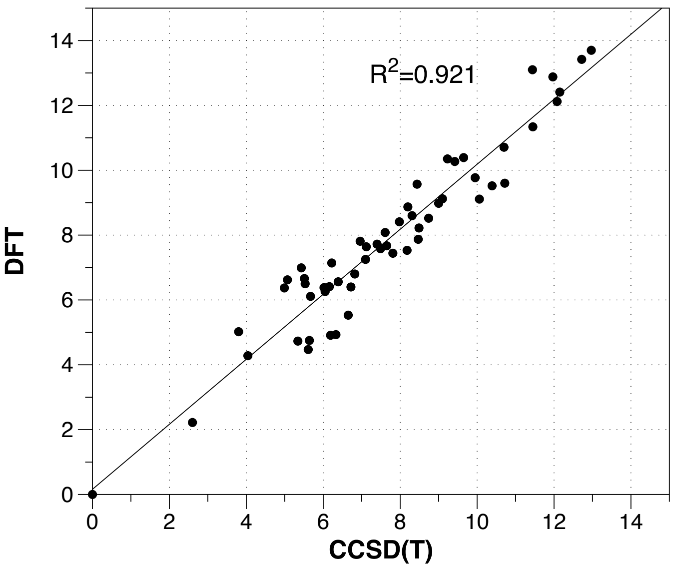

Fig. S1 Correlation of ωB97X-D/cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ relative energies, without zero-point energy correction, for the 7-11 most stable structures of each of the seven families. Relative energies are given in kJ.mol^{-1}.

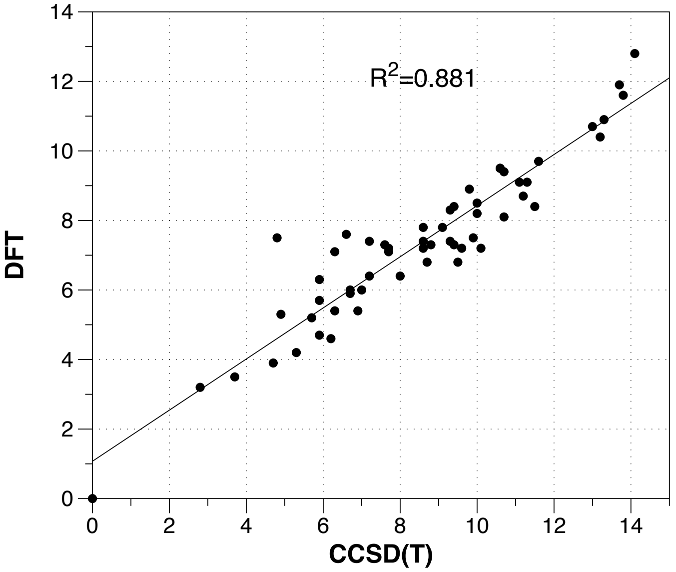

Fig. S2 Correlation of ωB97X-D/cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ relative energies, with zero-point energy correction, for the 7-11 most stable structures of each of the seven families. Relative energies are given in kJ.mol^{-1}.

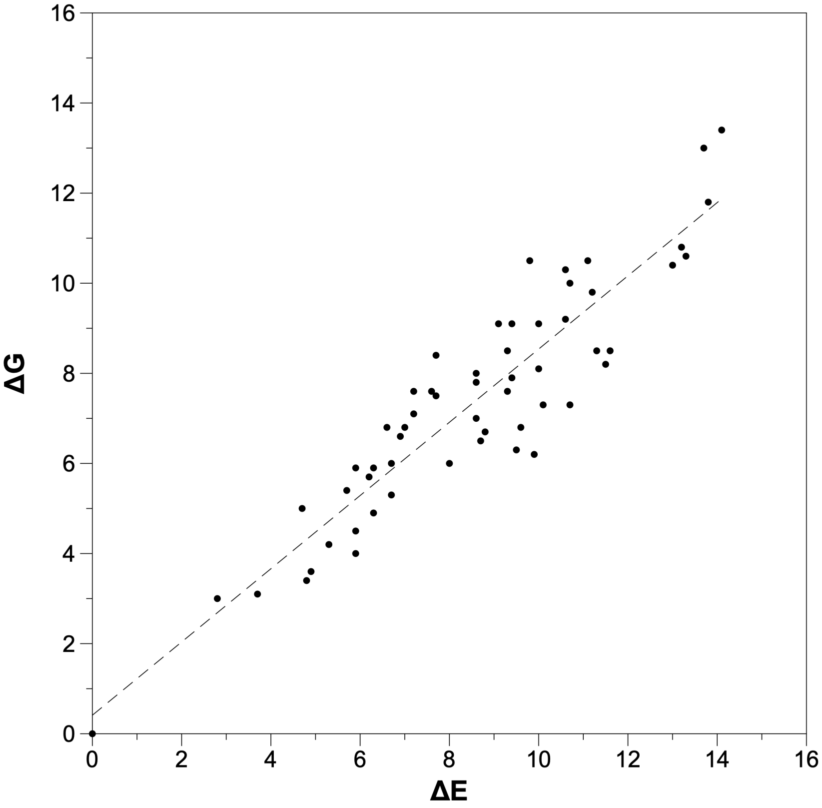

Fig. S3 Correlation between relative energies at 0 K and free energies at 298 K at the ωB97X-D/cc-pVTZ level. Relative energies are given in kJ.mol^{-1}.

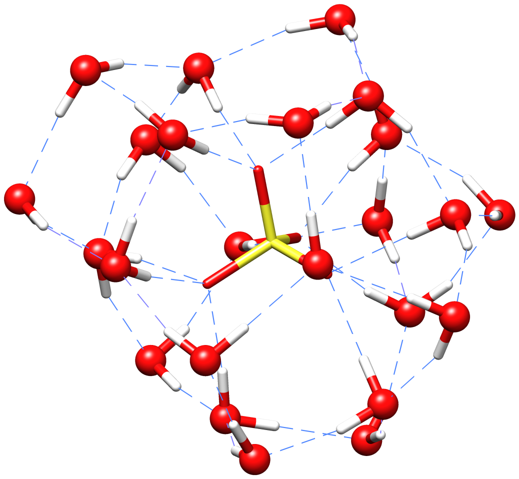

Fig. S4 Structure of the **W24-5** family.

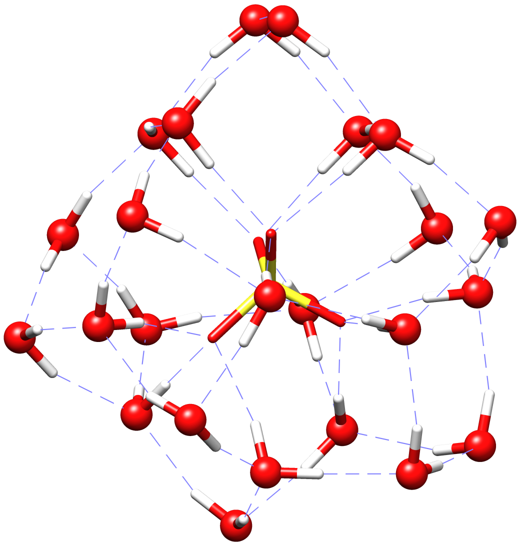

Fig. S5 Structure of the **W24-6** family.

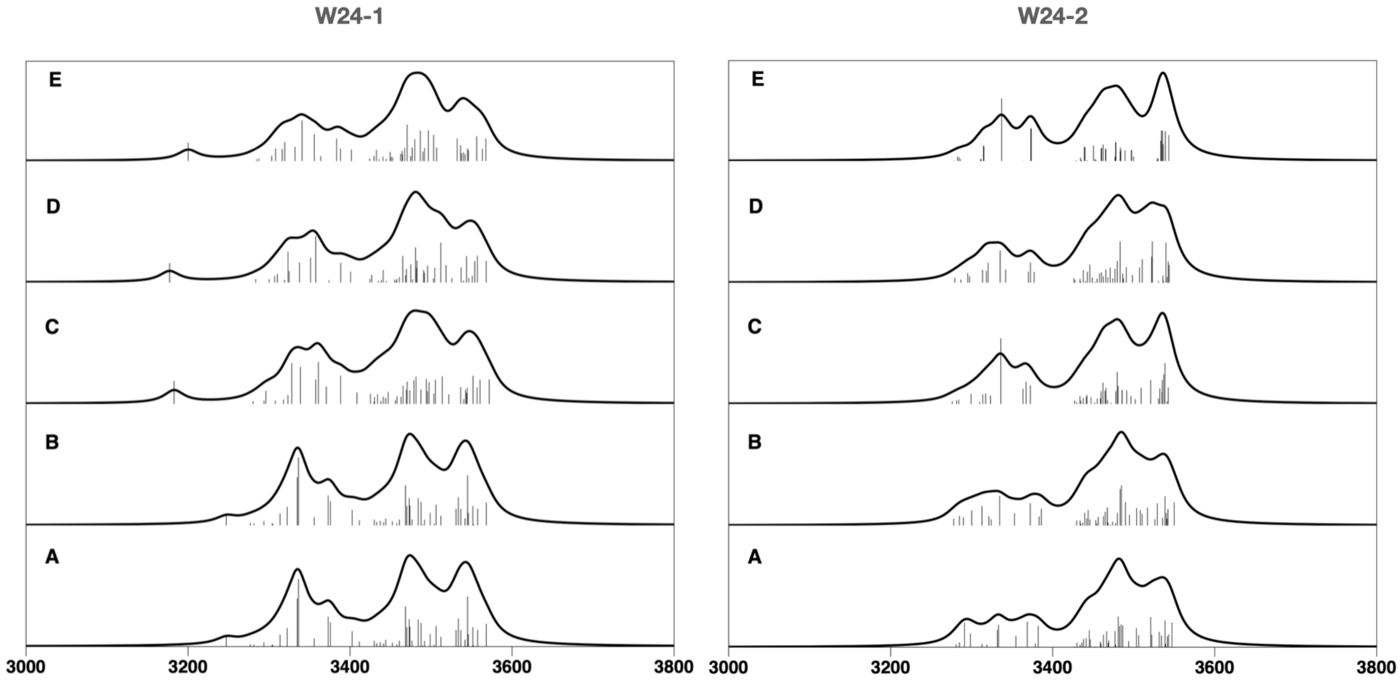

Fig. S6 IR spectra of the five most stable structures of **W24-1** and **W24-2** in the 3000-3800 cm^{-1} range.

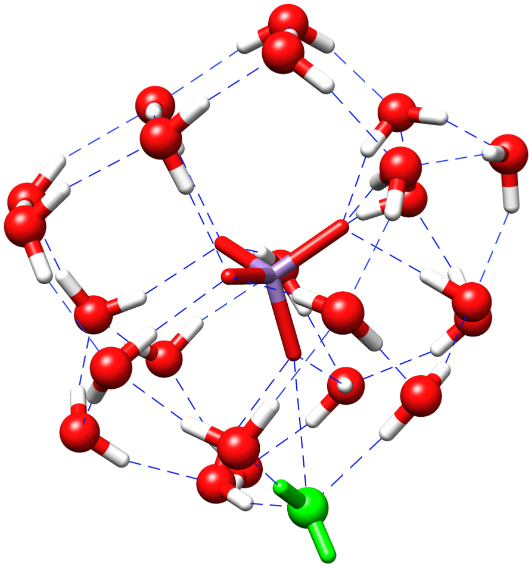

Fig. S7 A structure of $MnO_4^-(H_2O)_{24}$ from **W24-6** with one dangling O-H bond (green).