

## Supporting information

# Gas Phase Vibrational Spectroscopy of Microhydrated Sulfate Dianions $\text{SO}_4^{2-}(\text{H}_2\text{O})_{3-8}$

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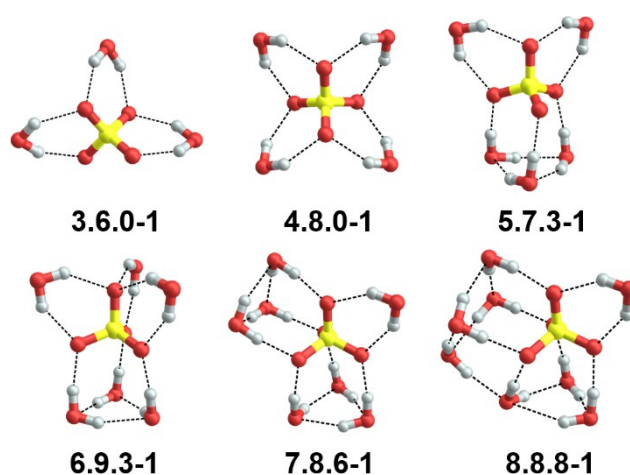
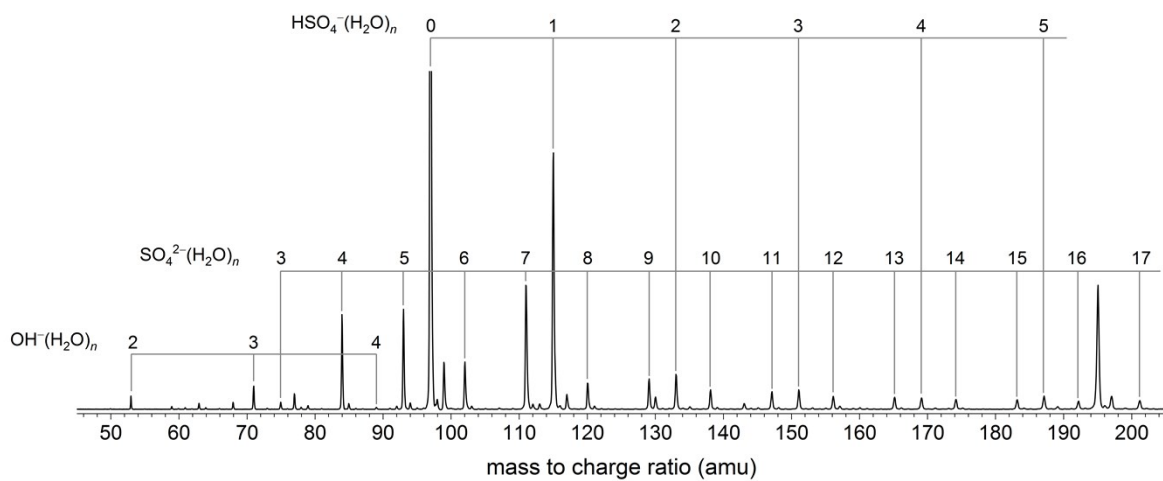
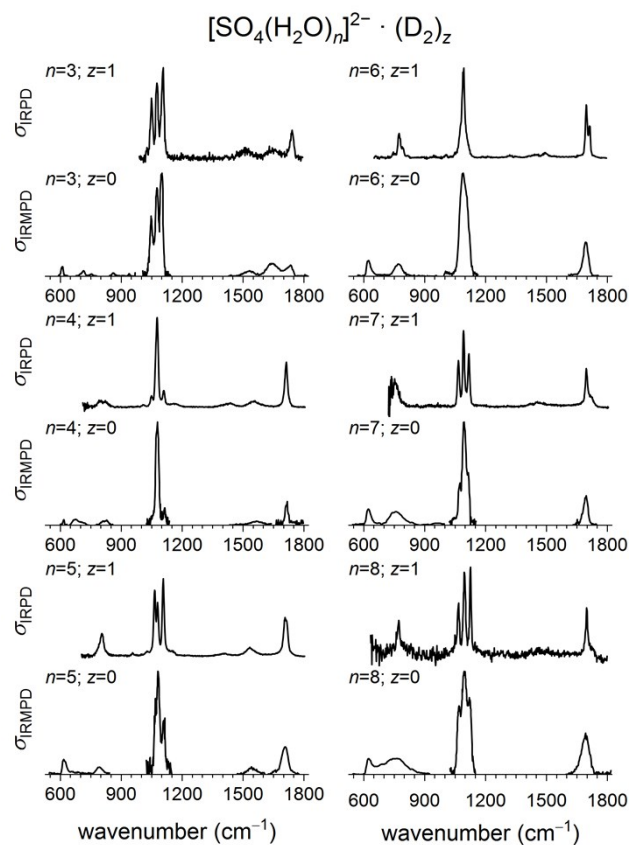


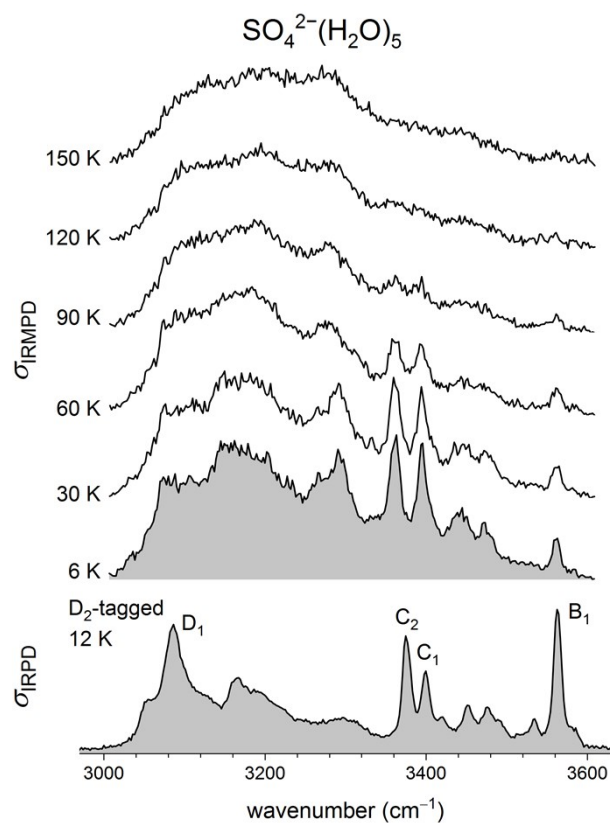
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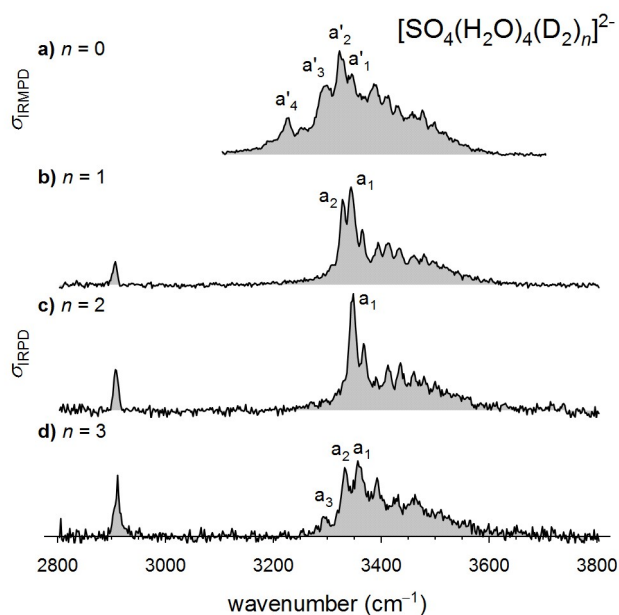
**Figure S1:** Quadrupole mass spectrum of a 20 mMol sulphuric acid in 50:50 water/acetonitrile solution.



**Figure S2:** Comparison of the IRPD spectra of  $\text{D}_2$ -tagged  $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$  ( $z = 1$ , present study) to IRMPD spectra of bare  $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$  dianions ( $z = 0$ , from Ref.)<sup>1</sup> for  $n = 3$  to 8 in the mid-IR spectral region.

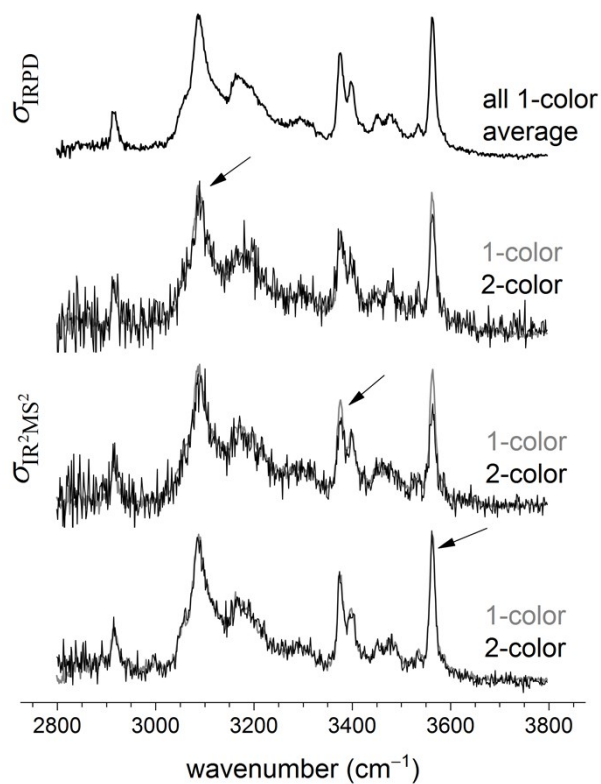


**Figure S3:** IRMPD spectra of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_5$  for trap temperatures from 6 to 150 K. For comparison the IRPD  $\text{D}_2$ -tagged spectrum of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_5$  is shown beneath.



**Figure S4:** a) IRMPD spectra compared with b)-d) IRPD spectra of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_4$  with different numbers of tagging molecules.

VPT2 calculations indicate that everything above  $a_1$  are combination bands of OH stretching vibrations with low-energy vibrations of water molecules. Quantum chemical calculations with  $\text{D}_2$  at different positions of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_4$ , prefer with about 2 kJ/mol, the oxygen of sulfate. We suspect that the second  $\text{D}_2$  molecule attaches to the opposite oxygen atom of the sulfate, leading to a higher molecule symmetry, explaining that  $a_2$  is no longer present. The situation for the third  $\text{D}_2$  molecule is probably different because the splitting between  $a_1$  and  $a_2$  is greater and a new peak  $a_3$  is observed, therefore we assume that the third  $\text{D}_2$  molecule attaches to one of the four oxygen of an  $\text{H}_2\text{O}$ . For the multiphoton spectrum we assume to have a second isomer.



**Figure S5:** Isomer-selective IRPD spectra (IR<sup>2</sup>MS<sup>2</sup>) of D<sub>2</sub>-tagged SO<sub>4</sub><sup>2-</sup>(H<sub>2</sub>O)<sub>5</sub> probed on three distinct absorptions indicating by an arrow. The corresponding IRPD spectrum is highlighted in grey.

**Table S1:** Experimentally determined values (in  $\text{cm}^{-1}$ ) of the antisymmetric SO stretch vibrations ( $\nu_{1-3}$ ), the mean of the frequencies ( $\bar{x}$ ), the spectral mean ( $\bar{x}_s$ ), the width ( $\Delta x$ ), and the spectral width ( $\Delta x_s$ ) for  $[\text{SO}_4(\text{H}_2\text{O})_n]^{2-}$ .

$n$	$\nu_1$	$\nu_2$	$\nu_3$	$\bar{x}$	$\bar{x}_s$	$\Delta x$	$\Delta x_s$
3	<b>1049</b>	<b>1076</b>	<b>1104</b>	1077	1087	56	72
4	<b>1076</b>			1076	1077	0	25
5	<b>1063</b>	<b>1079</b>	<b>1106</b>	1083	1081	43	60
6	<b>1089</b>			1089	1089	0	52
7	<b>1065</b>	<b>1092</b>	<b>1116</b>	1091	1092	51	62
8	<b>1065</b>	<b>1094</b>	<b>1124</b>	1094	1097	59	74

$$\bar{x} = \frac{\nu_1 + \nu_2 + \nu_3}{3}$$

$$\Delta x = \nu_3 - \nu_1$$

The spectral mean is defined by the integral of the cross section in such a way that the areas on both sides are equal.

$$\bar{x}_s = \frac{\int_a^b \nu \sigma(\nu) d\nu}{\int_a^b \sigma(\nu) d\nu}$$

$$\int_{\bar{x}_s - \frac{1}{2}\Delta x_s}^{\bar{x}_s + \frac{1}{2}\Delta x_s} \sigma(\nu) d\nu = 0.9 \int_a^b \sigma(\nu) d\nu$$

Cosine similarity is used to objectively assess the agreement between calculated and measured spectra. This is a measure for the similarity of two vectors, which is calculated as follows:

$$S = \frac{\sum a_i \cdot c_i}{\sqrt{\sum a_i^2} \cdot \sqrt{\sum c_i^2}}$$

The intensities of the IRPD spectrum are interpreted as vector  $a_i$  and the intensities of the calculated spectrum are interpreted as vector  $c_i$ .  $S$ -values close to one indicates high agreement, whereas values close to zero indicate bad agreement.

The value for  $S$  given in the following tables refers only to the sulfate stretching vibrations ( $1000$  to  $1200 \text{ cm}^{-1}$ ), as these do not show any pronounced anharmonicities.





**Table S2:** Relative electronic energies, relative zero point corrected energies and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies spectra for  $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$  isomers. All energies are in kJ/mol.

(a) B3LYP+GD3BJ/6-311++G(3df,3pd)

(b) CCSD(T)/CBS\* (taken from literature)<sup>2</sup>

(c) B3LYP /6-311++G(3df,3pd) (taken from literature)<sup>2</sup>

Isomer	$E_{\text{el}}(\text{a})$	$E_{\text{el}}(\text{b})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{c})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{a})$	$S$
3.3.3-1	0.0	4.8	10.1	10.7	0.3450
3.4.2-1	12.7	15.2	16.0	17.2	0.4210
3.5.1-1	3.8	2.6	5.4	5.2	<b>0.9230</b>
3.5.1-2	3.5	2.5	3.6	5.1	0.7876
3.5.1-3	10.1	10.2	11.1	12.4	0.1967
3.5.1-4	11.8	11.1	11.2	11.3	0.6599
3.6.0-1	2.9	0.0	<b>0.0</b>	<b>0.0</b>	<b>0.8975</b>
3.6.0-2	4.5	1.3	1.3	1.2	0.1569
3.6.0-3	5.1	2.4	1.7	2.1	0.6624

**Table S3:** Relative electronic energies, relative zero point corrected energies and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies spectra for  $\text{SO}_4^{2-}(\text{H}_2\text{O})_4$  isomers. All energies are in kJ/mol.

(a) B3LYP+GD3BJ/6-311++G(3df,3pd)

(b) CCSD(T)/CBS\* (taken from literature)<sup>2</sup>

(c) B3LYP/6-311++G(3df,3pd) (taken from literature)<sup>2</sup>

Isomer	$E_{\text{el}}(\text{a})$	$E_{\text{el}}(\text{b})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{c})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{a})$	$S$
4.4.4-1	6.6	9.3	15.3	17.1	0.4484
4.5.3-1	0.0	0.0	2.8	4.9	0.4230
4.5.3-2	8.4	8.9	12.2	14.4	0.0936
4.6.2-1	10.4	6.7	8.1	9.1	0.5475
4.6.2-2	8.3	5.1	6.7	8.5	0.5065
4.6.2-3	8.4	6.4	7.4	9.9	0.4484
4.7.1-1	7.2	1.6	<b>0.0</b>	2.3	0.3151
4.7.1-2	7.3	1.8	<b>0.5</b>	2.4	0.4929
4.7.1-3	11.7	n.a.	n.a.	n.a.	0.2193
4.8.0-1	8.7	2.1	1.3	<b>0.0</b>	<b>0.9906</b>
4.8.0-2	10.1	3.1	<b>0.3</b>	<b>0.7</b>	0.3929

**Table S4:** Relative electronic energies, relative zero point corrected energies and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies spectra for  $\text{SO}_4^{2-}(\text{H}_2\text{O})_5$  isomers. All energies are in kJ/mol.

(a) B3LYP+GD3BJ/6-311++G(3df,3pd)

(b) CCSD(T)/CBS\* (taken from literature)<sup>2</sup>

(c) B3LYP/6-311++G(3df,3pd) (taken from literature)<sup>2</sup>

Isomer	$E_{\text{el}}$ (a)	$E_{\text{el}}$ (b)	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{c})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{a})$	S
5.6.4-1	2.0	4.6	8.0	7.8	0.3364
5.6.4-2	2.1	4.7	7.3	7.9	0.3859
5.6.4-3	2.1	5.7	8.6	9.1	0.3399
5.6.4-4	1.2	4.1	6.5	6.9	0.3323
5.6.4-5	0.8	3.6	5.6	6.4	0.3308
5.6.4-6	1.6	5.6	8.0	8.4	0.2829
5.6.4-7	3.3	6.4	9.7	9.5	0.3201
5.7.3-1	0.0	0.0	0.6	<b>0.0</b>	<b>0.8869</b>
5.7.3-2	5.3	5.7	6.7	6.3	0.3121
5.7.3-3	19.0	n.a.	n.a.	n.a.	0.4629
5.8.2-1	9.2	n.a.	n.a.	n.a.	0.5991
5.9.1-1	10.8	5.8	<b>0.0</b>	0.8	0.7032
5.10.0-1	15.1	9.2	3.5	0.8	0.6798

**Table S5:** Relative electronic energies, relative zero point corrected energies and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies spectra for  $\text{SO}_4^{2-}(\text{H}_2\text{O})_6$  isomers. All energies are in kJ/mol.

(a) B3LYP+GD3BJ/6-311++G(3df,3pd)

(b) CCSD(T)/CBS\* (taken from literature)<sup>2</sup>

(c) B3LYP/6-311++G(3df,3pd) (taken from literature)<sup>2</sup>

Isomer	$E_{\text{el}}(\text{a})$	$E_{\text{el}}(\text{b})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{c})$	$E_{\text{el}}(\text{b})+E_{\text{ZP}}(\text{a})$	$S$
6.6.5-1	15.5	n.a.	n.a.	n.a.	0.2612
6.6.6-1	0.0	0.0	6.7	5.3	0.3239
6.6.6-2	0.6	0.8	7.8	6.3	0.3200
6.6.6-3	4.7	n.a.	n.a.	n.a.	0.3864
6.6.6-4	9.9	n.a.	n.a.	n.a.	0.4782
6.6.6-5	13.0	n.a.	n.a.	n.a.	0.4123
6.6.6-6	33.4	n.a.	n.a.	n.a.	0.0861
6.7.5-1	3.0	2.1	8.3	6.4	0.3876
6.7.5-3	4.5	4.1	9.7	8.1	0.4015
6.7.5-5	8.4	4.3	8.6	6.2	0.3378
6.7.5-7	7.7	n.a.	n.a.	n.a.	0.4566
6.7.5-8	9.0	n.a.	n.a.	n.a.	0.4222
6.7.5-9	11.8	n.a.	n.a.	n.a.	0.3137
6.7.5-10	14.8	n.a.	n.a.	n.a.	0.3374
6.7.5-11	14.3	n.a.	n.a.	n.a.	0.2597
6.7.5-12	13.9	n.a.	n.a.	n.a.	0.4116
6.7.5-13	19.5	n.a.	n.a.	n.a.	0.2318
6.7.5-14	20.5	n.a.	n.a.	n.a.	0.2536
6.8.4-1	8.7	3.5	5.9	4.3	0.7906
6.8.4-3	9.8	4.8	6.8	5.5	0.4655
6.8.4-5	8.4	2.8	4.1	2.9	0.8709
6.8.4-6	8.8	3.3	5.1	3.6	0.8759
6.8.4-9	8.7	n.a.	n.a.	n.a.	0.6255
6.8.4-10	9.4	n.a.	n.a.	n.a.	0.7794
6.8.4-11	14.4	n.a.	n.a.	n.a.	0.3880
6.8.4-12	14.4	n.a.	n.a.	n.a.	0.4564
6.8.4-13	15.7	n.a.	n.a.	n.a.	0.8174
6.8.4-14	16.3	n.a.	n.a.	n.a.	0.6288
6.8.4-15	18.4	n.a.	n.a.	n.a.	0.5545
6.8.4-16	17.8	n.a.	n.a.	n.a.	0.5158
6.8.4-17	21.2	n.a.	n.a.	n.a.	0.4138
6.8.4-18	21.0	n.a.	n.a.	n.a.	0.3342
6.8.4-19	19.6	n.a.	n.a.	n.a.	0.8690
6.9.3-1	11.1	3.2	<b>0.0</b>	<b>0.0</b>	<b>0.9493</b>
6.9.3-2	20.3	n.a.	n.a.	n.a.	0.5490
6.9.3-3	20.8	n.a.	n.a.	n.a.	0.6495
6.12.0-1	30.3	17.5	5.8	5.7	0.7330

**Table S6:** Relative energies of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_7$  isomers (all in kJ/mol) and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies at B3LYP+GD3BJ/6-311++G(3df,3pd) level of theory. The labels given here no longer correspond to those of Lambrecht *et al.*<sup>3</sup> due to methodical mistakes we have re-labeled them.

Isomer	$E_{\text{el}}$	$E_{\text{el}} + E_{\text{ZP}}$	$S$
7.6.7-1	0.0	0.0	0.4088
7.6.7-2	9.5	7.6	0.4208
7.7.7-1	3.0	2.4	0.3407
7.7.7-2	3.2	2.6	0.3404
7.7.7-3	14.3	11.6	0.2409
7.7.7-4	21.1	15.6	0.2550
7.8.6-1	4.4	0.5	<b>0.9043</b>
7.8.6-2	5.0	1.2	0.8976
7.8.6-3	7.2	4.6	0.4813
7.8.6-4	7.4	3.5	0.8605
7.8.6-5	7.5	5.0	0.4025
7.8.6-6	7.9	5.2	0.3685
7.8.6-7	8.1	4.2	0.6398
7.8.6-8	10.6	7.0	0.4217
7.8.6-9	11.3	7.2	0.5937
7.8.6-10	11.6	7.5	0.3762
7.8.6-11	12.5	8.4	0.5010
7.8.6-12	13.0	7.1	0.8697
7.8.6-13	13.1	8.2	0.6702
7.8.6-14	13.9	9.1	0.4176
7.8.6-15	16.8	12.5	0.2277
7.8.6-16	17.0	13.6	0.2105
7.8.6-17	19.2	13.5	0.5147
7.8.6-18	20.0	14.7	0.3773
7.8.6-19	20.4	14.5	0.6113
7.8.6-20	23.1	16.0	0.3120
7.8.6-21	37.5	29.0	0.2619
7.9.5-1	8.1	2.5	0.7935
7.9.5-2	9.2	3.6	0.3574
7.9.5-3	13.7	7.7	0.7320
7.9.5-4	14.3	6.2	0.7969
7.9.5-5	15.7	9.1	0.6687
7.9.5-6	15.7	8.5	0.7637
7.9.5-7	16.0	9.4	0.8223
7.9.5-8	19.2	11.1	0.4759
7.9.5-9	21.4	14.3	0.6849
7.10.4-1	16.6	7.3	0.7962
7.11.2-1	40.5	22.4	0.7176
7.12.2-1	36.0	18.6	0.7628

**Table S7:** Results for the relative energies of  $\text{SO}_4^{2-}(\text{H}_2\text{O})_8$  isomers (all in kJ/mol) and value for the cosine similarity between the IRPD spectrum and calculated harmonic frequencies calculated at B3LYP+GD3BJ/6-311++G(3df,3pd) level of theory.

Isomer	$E_{\text{el}}$	$E_{\text{el}} + E_{\text{ZP}}$	$S$
8.7.9-1	5.6	5.7	0.4152
8.7.9-2	6.5	6.1	0.6417
8.7.9-3	6.6	6.1	0.6607
8.7.9-4	4.3	6.8	0.4610
8.7.9-5	6.8	7.6	0.4570
8.8.8-1	1.2	0.0	0.7267
8.8.8-2	1.5	0.3	0.5606
8.8.8-3	0.0	1.3	0.5714
8.8.8-4	0.8	1.8	0.3534
8.8.8-5	0.8	1.9	0.3029
8.8.8-6	1.1	2.2	0.4451
8.8.8-7	3.0	4.7	0.5107
8.8.8-8	4.7	5.2	0.5181
8.9.7-1	7.3	5.0	0.5256
8.9.7-2	6.6	5.1	<b>0.9566</b>
8.9.7-3	7.5	5.2	<b>0.9572</b>
8.9.7-4	10.9	8.1	0.2214
8.9.7-5	10.8	8.2	0.5225
8.9.7-6	11.3	9.4	0.6476
8.9.7-7	11.6	9.8	0.4535
8.9.7-8	13.0	10.8	0.5054
8.11.5-1	29.3	18.2	0.4650
8.12.4-1	41.5	25.7	0.5091
8.12.4-2	46.3	30.2	0.8589

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3. D.S. Lambrecht, G.N.I. Clark, T. Head-Gordon and M. Head-Gordon, *J. Phys. Chem. A*, 2011, **115**(41), 11438.