Supplemental Material

to

Evidence for the Blue 10π S_6^{2+} Dication in Solutions of $S_8(AsF_6)_2$: A Computational Study including Solvation energies.

by

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1. Discussion of the Calculated Sulfur Cation Geometries

Three S_3^+ Isomers

At the B3PW91/6-311+G(3df) level of theory, the most favorable S_3^+ cation is a 2B_2 state [$d(S-S) = 1.911 \text{ \AA}$, $S-S-S = 101.4^\circ$], followed very closely ($E_{\text{rel.}} = 0.30 \text{ kJ/mol}$), by the 2A_1 state with a relaxed $S-S-S$ bond angle of 130.6° and a shorter $S-S$ distance of $1.872 \text{ \AA}$. The same relative order was found earlier, however, only for the relaxed, adiabatic states. Vertical ionisation favors the 2A_1 state^[1]. The Mulliken charges of both C_{2v} species are nearly evenly distributed while the spin densities clearly reside on the two terminal atoms. The third C_s -symmetric $^2A'$ isomer is close in energy and only 6.84 kJ/mol less favorable than the 2B_2 state [$^2A'$: $d(S-S) = 1.869; 1.992 \text{ \AA}$; $S-S-S = 112.0^\circ$]. The highest Mulliken charges reside on the central and the terminal sulfur atom with the longer $S-S$ distance. All three isomers are true minima without imaginary frequencies and are in good agreement with earlier calculations^[1].

Triangular S_3^{2+} (D_{3h})

As shown earlier, S_3^{2+} has a triangular geometry and a triplet ground state^[2]. Therefore, we repeated the optimization of triplet S_3^{2+} at the B3PW91/6-311+G* level of theory. Our computed $S-S$ distance of $2.036 \text{ \AA}$ compares well to Schaefer's earlier finding that concluded to a "best" value of about $2.03 \text{ \AA}$ ^[2].

Square planar S_4^+ (D_{4h})

It was found that the D_{4h} square is clearly the global minimum on the S_4^+ hypersurface^[1] which is in contrast to the very complex neutral S_4 hypersurface^[3]. We therefore used this symmetry restriction to optimize the geometry of S_4^+ and found a true minimum with $S-S$ bond lengths of $2.058 \text{ \AA}$ and delocalized charges and spin densities. The $S-S$ distance in the 7π aromatic S_4^+ is longer than in the 6π aromatic S_4^{2+} computed at the same level ($2.016 \text{ \AA}$) or experimentally observed [$2.011(3) \text{ \AA}$]^[4d,5].

C_s-symmetric S₅⁺

The optimization of S₅⁺ proceeded initially in C₁ symmetry which led to a true minimum close to C_s symmetry. Therefore cyclic S₅⁺ was reoptimized employing this symmetry restraint. However, the resulting geometry is only slightly lower in energy (~1 kJ/mol) and a true minimum (²A"). Starting at the envelope top, a short-long-short bond alternation of 2.034, 2.076 and 2.021 Å is found. The Mulliken charges are evenly spread over all 5 sulfur atoms but the spin densities are mainly located in the plane formed by the four atoms excluding the one at the envelope top. This geometry is in very good agreement with earlier findings^[1]. We also optimized S₅⁺ in C₂ symmetry, however, this led to a transition state (30i cm⁻¹) that was 23 kJ/mol higher in energy than the C_s isomer (6-311+G(3df) basis set; only 0.41 kJ/mol with the 6-311+G* basis!).

D_{3d}-symmetric S₆

The solid state geometry of S₆ was shown to consist of a six-membered ring in the chair conformation with local D_{3d} symmetry^[6]. We optimized S₆ using this point symmetry and the optimization converged giving a S-S distance of 2.061 Å, a S-S-S bond angle of 103.0° and a S-S-S-S torsion angle of 73.1°. This is very close to earlier computational findings (2.064 Å at HF/3-21G*)^[7] and the experimental determination which gives d(S-S) as 2.068 Å, S-S-S as 102.6° and S-S-S-S as 73.8°^[8].

D_{3d}-symmetric S₆⁺

No previous report on the S₆⁺ geometry is available. However, only two geometries are assumed to be likely candidates for the global minimum of S₆⁺: a six-membered ring (D_{3d}) in the chair conformation as found experimentally in neutral S₆ and one in the boat conformation (C_{2v}) as is observed in the respective, heavier Te₆²⁺ dication in [Te₆][MOCl₄]₂ (M = W, Nb)^[9]. The optimization of S₆⁺ in D_{3d} symmetry proceeds smoothly and leads to a true minimum with a S-S bond length of 2.044 Å, a S-S-S bond angle of 108.5° and a S-S-S-S torsion angle of 62.4°. The six-membered ring in S₆⁺ is less puckered than in neutral S₆, the S-S bond distance is shorter by 2.4 pm and positive charges and spin densities are delocalised over all atoms. The optimization in C_{2v} symmetry led to a transition state which is not discussed here.

D_{3h} symmetric S₆⁴⁺

In analogy to the experimentally well known Te₆⁴⁺ cation [in Te₆(AsF₆)₄]^[10] the geometry of S₆⁴⁺ was optimized as an elongated trigonal prism in D_{3h} symmetry and as a singlet (since the ready observation of an ordinary ¹²⁵Te-NMR spectrum of Te₆⁴⁺). This species was briefly mentioned in earlier work^[11]. The optimization led to a true minimum with a S-S distance of 2.051 Å in the triangular faces but a long separation of 2.821 Å between the triangles. This may be compared to the earlier findings at the HF/DZ(p) level of theory which gives very similar values of 2.037 and 2.775 Å. However, in Te₆⁴⁺ the separation between the triangles exceeds that within the triangles only by 0.458 Å or 17 % while in our calculated S₆⁴⁺ geometry this difference amounts to 0.770 Å or 37 %. This is attributed to the increased Coulomb repulsion due to shorter S-S bond lengths between the two doubly charged S₃²⁺ units in this lighter homologue of Te₆⁴⁺ (cf. the separation in Te₆⁴⁺ is 3.06 to 3.13 Å).

C₁ (C₂)-symmetric S₇⁺

First attempts to optimize S₇⁺ were done using the C_s symmetric structure of neutral S₇. However, the frequency analysis showed one slightly imaginary vibration (22 i cm⁻¹). Lowering the

symmetry according to the movement of this vibration led to a true minimum, which is only 1 kJ/mol lower in energy but structurally very different. This nearly C_2 symmetric S_7^+ geometry can be derived from a six membered ring in the chair conformation, where one edge of the central four, coplanar atoms is bridged by a sulfur atom so that five atoms are in one plane. These five coplanar atoms bear nearly all the positive charge (Mulliken) and all the spin densities. A pronounced bond length alternation is observed (2.054; 2.027; 2.076 and 2.025 Å starting at the sulfur atom S7 which incorporates the twofold axis). A similar conformation and bond lengths alternation in the seven membered ring is found in the two seven membered rings of the S_{19}^{2+} dication in the solid state structure of $S_{19}(SbF_6)_2$, compared in S-S-Figure 1^[12].

S-Figure 1: Comparison of the computed S_7^+ geometry and one S_7 ring in the experimental structure of $S_{19}(SbF_6)_2$.

The bond lengths around the tricoordinated sulfur atom in the S_{19}^{2+} structure^[12] are longer than those calculated for S_7^+ , but this is attributed to the tricoordination. The two seven membered rings in the experimental S_{19}^{2+} structure are connected to the S_5 bridge at the position with the highest spin density in the calculated S_7^+ cation (0.40, S7 in S-S-Figure 1).

C_1 (C_2)-symmetric S_{10}^{2+}

Due to the large size of the calculation only one isomer of the S_{10}^{2+} dication, which has not been calculated previously, was fully optimized. The starting geometry of S_{10}^{2+} was derived by scaling the experimentally known Se_{10}^{2+} solid state structure by 0.87. The optimization proceeded without any symmetry restraints but the calculated minimum geometry exhibits perfect C_2 symmetry as found previously in the experimental Se_{10}^{2+} solid state structures in $[Se_{10}][A]$ ($A = SbF_6^-, SO_3F^-$)^[13]. In E_{10}^{2+} ($E = S, Se$) a six membered ring in the boat conformation is bridged in the 1 and 4 position by a four membered E_4 chain resulting in two tricoordinated chalcogen atoms which formally bear the positive charge. Computed sulfur and experimental selenium geometries exhibit a very pronounced bond lengths variation [$d(S-S) = 1.951$ - 2.242 Å] with very long E-E bonds around the two tricoordinated chalcogen atoms (2.148 to 2.242 Å) and the central E-E bond in the E_4 bridge (2.147 Å). The short bonds of 1.951 and 1.972 Å are nearly in the range S-S double bonds [cf. $d(S=S)$ in S_2 is 1.889 Å, $d(S-S)$ in S_8 is 2.060 Å (exp.)]. The two E_2 and one E_4 bridges show a marked long-short-long and long-short-long-short-long bond lengths alternation (starting at the tricoordinated E-atoms). In addition to the marked bond lengths alternation a charge alternation is found in the calculated Mulliken charges of S_{10}^{2+} with the tricoordinated S1 and S8 (+0.95) as well as the S2, S6, S7 and S10 atoms (+0.15 to +0.32) bearing a positive charge but the rest (S3, S4, S5, S9) bearing a negative charge (-0.18 to -0.23).

S-Table 1: Total energies of assessed species.

Parameter	S ₁₀ ²⁺	S ₈	S ₈ ²⁺	S ₆ ²⁺	S ₄ ²⁺	S ₃ ²⁺	S ₆ ⁴⁺
Row 1: Gas Phase 0K: B3PW91/6-311+G*	-3980.9104	-3185.35542	-3184.55181	-2388.17336	-1591.78727	-1193.54589	-2386.5698
Row 2: Free Energy at 298K incl. ZPE at the B3PW91/6-311+G(3df)//B3PW91/6-311+G* Level	-3981.06841	-3185.47613	-3184.69551	-2388.28658	-1591.87598	-1193.61455	-2386.7041
Row 3: Δ(row1-row2) = correction to solvated values at the B3PW91/6-311+G* level in row 4-6!	-0.1580182	-0.1207071	-0.1437027	-0.1132252	-0.0887049	-0.068658	-0.134232
Row 4: SCIPCM: B3PW91/6-311+G* (DC = 14)		-3185.35696	-3184.83058	-2388.47346	-1592.13083	-1193.91451	-2387.7759
Row 5: SCIPCM: B3PW91/6-311+G* (DC = 83)			-3184.84917	-2388.49375			
Row 6: SCIPCM: B3PW91/6-311+G* (DC = 110)			-3184.85012	-2388.49503			

S-Table 1, continued: Total energies of assessed species.

Parameter	S ₂ ⁺	S ₃ ⁺	S ₄ ⁺	S ₅ ⁺	S ₆ ⁺	S ₇ ⁺
Row 1: Gas Phase 0K: B3PW91/6-311+G*	-795.95317	-1194.10778	-1592.31038	-1990.50298	-2388.67763	-2786.85351
Row 2: Free Energy at 298K incl. ZPE at the B3PW91/6-311+G(3df)//B3PW91/6-311+G* Level	-795.99598	-1194.17313	-1592.39032	-1990.59843	-2388.78394	-2786.97266
Row 3: Δ(row1-row2) = correction to solvated values at the B3PW91/6-311+G* level in row 4-6!	-0.0428053	-0.065348	-0.0799453	-0.0954528	-0.1063112	-0.1191459
Row 4: SCIPCM: B3PW91/6-311+G* (DC = 14)	-796.05588	-1194.20112	-1592.40235	-1990.58745	-2388.75783	-2786.93204
Row 5: SCIPCM: B3PW91/6-311+G* (DC = 83)			-1592.40871	-1990.59311		-2786.93739
Row 6: SCIPCM: B3PW91/6-311+G* (DC = 110)			-1592.40903	-1990.59339		-2786.93766

2. The calculation of stretching and bending mode scaling factors for S_6

Scaling all calculated bending (stretching) modes of S_6 for best fit to the experimental values leads to scaling factors of 1.031 (1.062) (see S-Table 2).

S-Table 2: Comparison of experimental and computed vibrational frequencies of S_6 .

S_6 unscaled	S_6 exp. sym.	S_6 Scaled	sf.
163 E_u	180	168	Bending Modes 1.031
198 E_g	203	204	
260 A_{1g}	265	268	
310 A_{2u}	312	320	
333 A_{1u}	390	354	Stretching Modes 1.062
427 E_g	451	453	
448 E_u	462	476	
468 A_{1g}	477	497	

B3PW91 reproduces all the symmetries of the vibrations experimentally assigned in a normal coordinate analysis. Our scaled vibrational frequencies reproduce the experimental values within +20 and -26 cm^{-1} and we find an (arithmetic) average deviation of 10.8 cm^{-1} .

3. Calculated vibrational spectra

S_6 is the only species calculated for which experimental data are also available, experimental modes of S_6 were assigned based on a Urey-Bradley force field. To judge the quality of our calculations and to verify our previously derived stretching mode scaling factor of 1.064 (>310 cm^{-1}) and bending mode scaling factor of 1.051 (< 310 cm^{-1}) at the B3PW91/6-311+G* level of theory we also assessed these properties for neutral S_6 . The derived stretching (bending) mode scaling factors (see supplemental for details) of 1.062 (1.031) are very close to these found for S_4^{2+} (1.064) and S_8^{2+} (1.064 and 1.051) and therefore we scaled the vibrational modes of all experimentally unknown S_n^+ ($n = 3 - 7$) and S_n^{2+} ($n = 3, 6, 10$) cations given below by 1.063 (stretches) and 1.041 (bends). The scaling factors greater than unity reflect the overestimation of the S-S bond length by 1.7 – 2.0% at the B3PW91/6-311+G* level of theory. All scaled frequencies are collected in S-Table 3 together with the symmetry of the vibration and the scaled (1.041) zero point energy (ZPE).

S-Table 3: Zero point energy ZPE and calculated scaled vibrational frequencies of S_6 and the most favorable S_n^{2+} ($n = 3-7$) and S_n^{3+} ($n = 3, 6, 8$) cations in cm^{-1} . Bending modes below 310 cm^{-1} were scaled by 1.041, stretching modes above 310 cm^{-1} by 1.063 (see text). The relative Raman intensities (in %) using the option freq=raman in G98W are given for selected species.

Species Sym.	S_3^+ (C_{3v})	S_3^{2+} (D_{3h})	S_4^+ (Int.) (D_{4h})	S_5^+ (Int.) (C_s)	S_6 (D_{3d})	S_6^+ (D_{3d})	S_6^{2+} (Int.) (D_{3d})	S_6^{4+} (D_{3h})	S_7^+ (Int.) (C_1)	S_8^{2+} (Int.) (C_s)	S_{10}^{3+} (C_1)
ZPE ^{a)}	8.30	9.27	15.12	18.84	24.47	23.14	23.50	24.93	27.05	33.05	40.53
			62 (0) B_{2u}	41 (5) A''	170 E_u	81 E_u	88 (0) E_u		42 (4)	88 (3)	80
Bending modes ^{b)}								128 E'	107 (2)	104 (28)	96
sf.=1.041	220 A_1			228 (7) A'	206 E_g	207 E_g	220 (26) E_g	136 A_1''	148 (19)	126 (37)	110
				285 (10) A'	271 A_{1g}	268 A_{1g}	258 (17) A_{1g}		151 (12)	146 (20)	124
			320 (18) B_{1g}		320 A_{2u}	301 A_{1u}	296 (0) A_{1u}	240 E''	186 (4)	164 (38)	159
									227 (8)	180 (2)	172
									240 (18)	217 (64)	194
									288 (41)	251 (36)	211
										270 (10)	212
Stretching modes ^{b)}				329 (25) A''							
sf.=1.063				359 (31) A'	354 A_{1u}	364 A_{2u}	403 (0) A_{2u}	405 E''	335 (90)	359 (3)	328
				378 (10) A''					446 (6)	451 (32)	335
				477 (6) A''	453 E_u	450 E_u	440 (100) A_{1g}		447 (100)	486 (11)	379
		487 E'	499 (0) E_u		476 E_g	473 A_{1g}	469 (0) E_u		497 (13)	491 (65)	400
	504 B_2			502 (100) A'	497 A_{1g}	473 E_g	477 (8) E_g		499 (1)	515 (100)	408
				541 (10) A'					513 (58)	516 (4)	543
										541 (60)	546
	659 A_1	679 A_1'	548 (100) A_{1g}					648 A_2''			565
			597 (42) B_{2g}					654 A_1''			572

^{a)} in kJ/mol , ^{b)} in cm^{-1} .

The calculated, scaled frequencies of the species in S-Table 3 range from 41 to 679 cm^{-1} and are generally close to the values calculated for S_8^{2+} . S_3^{2+} was previously examined computationally^[13] and at the best level employed [CISD/TZ(2p)] the E' mode was found at 501 cm^{-1} and the A_1' mode at 694 cm^{-1} . From an analysis of a range of calculated vibrational spectra of this species, the authors concluded to “most likely” experimental values of $505 \pm 15 \text{ cm}^{-1}$ (E') and $680 \pm 40 \text{ cm}^{-1}$ (A_1'). This is in very good agreement with our scaled values of 487 and 679 cm^{-1} . The scaled vibrational frequencies collected in S-Table 3 should be close to experimentally expected values and, therefore, will serve as guidance in the experimental detection of hitherto unknown S_n^+ and S_n^{2+} cations. However, comparison of the calculated Raman scattering activities of S_8^{2+} to the experimental Raman intensities [in $\text{S}_8(\text{AsF}_6)_2$]^[14] reveals an only very qualitative agreement between calculation and experiment. Roughly said, the computation overestimates the intensity of S-S stretches but underestimates the intensity S-S-S bends.

4. Additionally calculated possible dissociation reactions of the S_n^{2+} ($n = 4, 6, 8, 10$) dications

In the main text we concentrated on likely dissociation equilibria including S_6^{2+} and S_4^{2+} . Moreover we showed, experimentally and theoretically, that S_2^+ is unstable in solution towards dimerisation to give S_4^{2+} and therefore we removed all reactions containing S_2^+ from the main text and shifted it to the supplemental material.

S-Table 4: Reaction enthalpies and free energies of dissociation reactions of S_n^{2+} ($n = 4, 6, 8, 10$) and S_6^{4+} in the gas phase and in SO_2 solution at 298 K [in kJ/mol].

eq.	Dissociation Reactions of S_8^{2+} [kJ/mol]	$\Delta_r H^{298}$ theor.	$\Delta_r H^{298}$ exp. ^{a)}	$\Delta_r G^{298}$ theor.	$\Delta_r G^{298}(\text{SO}_2)$ theor.
(S-1)	$\text{S}_6^{4+}(\text{g}) \rightarrow 2 \text{S}_3^{2+}(\text{g})$	-1320	-	-1378	-147
(S-2)	$\text{S}_4^{2+}(\text{g}) \rightarrow 2/3 \text{S}_3^{2+} + 1/3 \text{S}_6^{2+}$	+103	+120	+98	+92
(S-3)	$\text{S}_4^{2+}(\text{g}) \rightarrow 1/3 \text{S}_6^{4+} + 1/3 \text{S}_6^{2+}$	+543	-	+548	+118
(S-4)	$\text{S}_4^{2+}(\text{g}) \rightarrow 2 \text{S}_2^+(\text{g})$	-258 ^{b)}	-	-308 ^{b)}	+58
(S-5)	$\text{S}_6^{2+}(\text{g}) \rightarrow 2 \text{S}_3^+(\text{g})$	-93	-	-157	+163
(S-6)	$\text{S}_6^{2+}(\text{g}) \rightarrow \text{S}_2^+(\text{g}) + \text{S}_4^+(\text{g})$	-212	-242	-262	+55
(S-7)	$\text{S}_8^{2+}(\text{g}) \rightarrow \text{S}_2^+(\text{g}) + \text{S}_6^+(\text{g})$	-167	-149 ^{c)}	-222	+33
(S-8)	$\text{S}_8^{2+}(\text{g}) \rightarrow \text{S}_2^+(\text{g}) + 0.5 [\text{S}_5^+(\text{g}) + \text{S}_7^+(\text{g})]$	-171	-175 ^{c)}	-226	+25
(S-9)	$\text{S}_8^{2+}(\text{g}) \rightarrow 0.5 \text{S}_4^{2+}(\text{g}) + \text{S}_6^+(\text{g})$	-39	-21 ^{c)}	-69	+2
(S-10)	$\text{S}_8^{2+}(\text{g}) \rightarrow 0.5 [\text{S}_4^{2+}(\text{g}) + \text{S}_5^+(\text{g}) + \text{S}_7^+(\text{g})]$	-43	-47 ^{c)}	-74	-6
(S-11)	$\text{S}_8^{2+}(\text{g}) \rightarrow 1/2 \text{S}_6^{2+}(\text{g}) + 1/2 \text{S}_{10}^{2+}(\text{g})$	+44	+41	+47	+21
(S-12)	$\text{S}_8^{2+}(\text{g}) + 2/8 \text{S}_8(\text{g}) \rightarrow \text{S}_{10}^{2+}(\text{g})$	-	-30	-	-
(S-13)	$\text{S}_{10}^{2+}(\text{g}) \rightarrow 2/3 \text{S}_8^{2+}(\text{g}) + 2/3 \text{S}_7^+(\text{g})$	-88	-78	-115	-42
(S-14)	$\text{S}_8^{2+}(\text{g}) + 1/8 \text{S}_8(\text{g}) \rightarrow \text{S}_4^+(\text{g}) + \text{S}_5^+(\text{g})$	-232	-253	-285	-13
(S-15)	$\text{S}_8^{2+}(\text{g}) + 2/8 \text{S}_8(\text{g}) \rightarrow 2 \text{S}_5^+(\text{g})$	-296	-298	-347	-58
(S-16)	$\text{S}_8^{2+}(\text{g}) + 4/8 \text{S}_8(\text{g}) \rightarrow \text{S}_5^+(\text{g}) + \text{S}_7^+(\text{g})$	-321	-312	-361	-55
(S-17)	$\text{S}_8^{2+}(\text{g}) + 6/8 \text{S}_8(\text{g}) \rightarrow 2 \text{S}_7^+(\text{g})$	-348	-325	-378	-55

^{a)} semi experimentally derived values [$\Delta_r H^{298}(\text{S}_n^+, \text{g})$: experimental values, $\Delta_r H^{298}(\text{S}_n^{2+}, \text{g})$: calculated values], ^{b)} from Reference [15,16], ^{c)} from Reference [14].

Thermodynamically $\text{S}_6^{2+}(\text{g})$, $\text{S}_8^{2+}(\text{g})$ and $\text{S}_{10}^{2+}(\text{g})$ could also dissociate by formation of smaller, doubly charged $\text{S}_n^{2+}(\text{g})$ ($n = 4, 6, 8$) and $\text{S}_n^+(\text{g})$ cations. Dissociations of $\text{S}_8^{2+}(\text{g})$ to give $\text{S}_6^{2+}(\text{g})$ and a $\text{S}_n^+(\text{g})$ cation are favored by 24 to 90 kJ/mol (eq. 16 and 17). The stability of $\text{S}_6^{2+}(\text{g})$ towards a

disproportionation to give $S_4^{2+}(g)$ and $S_8^{2+}(g)$ (eq. 11) is close to 0 kJ/mol, both for ΔH and ΔG . $S_6^{2+}(g)$ may also dissociate to give $S_4^{2+}(g)$ and a $S_n^+(g)$ cation ($n = 4, 5$, eq. 12 and 13). A dissociation reaction of $S_4^{2+}(g)$ into $S_3^{2+}(g)$ and $S_6^{2+}(g)$ is endothermic (endergonic) by at least 103 (98) kJ/mol. $S_8^{2+}(g)$ reacts very exothermic (exergonic) with elemental octasulfur $S_{8(g)}$ forming the $S_4^+(g)$, $S_5^+(g)$ and $S_7^+(g)$ radical cations (eq. S-14 to S-17). Reactions giving $S_6^+(g)$ are also favorable but $S_6^+(g)$ itself may be unstable towards a disproportionation to give $S_5^+(g)$ and $S_7^+(g)$ by 4 kJ/mol (eq. 21).

5. Extrapolated UV/Vis spectrum of S_8^{2+}

The UV-Vis absorption of S_4 was earlier calculated to occur at 500 nm (using CIS), 30 nm lower than the experimental value of 530 nm. Taking the last result as well as the calculated and experimental values of S_4^{2+} we therefore can define a scaling factor that allows us to convert the values of the calculated transitions into experimentally expected values. In the case of S_4 (S_4^{2+}) this would be 1.060 (1.065)^[17]. Similarly the experimental Se_8^{2+} spectrum can be scaled by the S_4^{2+}/Se_4^{2+} ratio of 330 nm/410 nm = 0.805 and 280 nm/320 nm = 0.875 (average: 0.840) to give the experimentally expected values of the transitions of the dissolved S_8^{2+} dication.

S-Table 5: Extrapolated UV/Vis spectra of S_8^{2+} .

Transition	scaled (1.063) calc. S_8^{2+} UV-Vis	scaled (0.840) exp. Se_8^{2+} UV-Vis
2 nd E.S.	561 (0.0713)	575 ($\epsilon = 400$)
3 rd E.S.	531 (0.0813)	
4 th E.S.	384 (0.1188)	395 ($\epsilon = 250$)
-	-	252 ($\epsilon = 900$)

According to the latter procedure, one would expect three transitions for S_8^{2+} at 575 nm ($\epsilon \sim 400$), 395 nm ($\epsilon \sim 470$) and 252 nm ($\epsilon \sim 900$) in agreement with earlier conclusions by Gillespie et al.^[18]. This may be compared to the scaled (by 1.063) computed spectrum which predicts two medium transitions at 561 ($f = 0.0713$) and 531 ($f = 0.0813$) nm and a strong transition at 384 nm ($f = 0.1188$). Computed and experimentally expected UV-Vis spectra of S_8^{2+} are in good qualitative agreement

6. Solvation Free Energies of Selected Cations Obtained by COSMO at the B3PW91/6-311+G* Level

Solvation Free Energies (COSMO-Model)	DC =14 [kJ/mol]
S_4^+	-209.62
S_5^+	-195.94
S_7^+	-176.02
S_6^{2+}	-719.82
S_8^{2+}	-662.41

7. Simulated UV-Vis spectra of stoichiometric mixtures of S_8^{2+} , S_6^{2+} and S_5^+

S-Figure 2: a) Simulated^[19] UV-Vis spectra of stoichiometric mixtures of S_8^{2+} , S_6^{2+} and S_5^+ ; b) simulated UV-Vis spectra of the isolated S_8^{2+} , S_6^{2+} and S_5^+ ions with intensities at an arbitrary scale.

References to the Supplemental Material

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- [17] By dividing the experimentally observed value with the calculated value, e.g. in S_4 : 530 nm/500 nm = 1.060, in S_4^{2+} : 330 nm/310 nm = 1.065.
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solution decreasing the effect of impurities and surface OH groups. Under these conditions some of the added AsF_5 has been used in reacting with traces of impurities in the SO_2 and with the surfaces, and the UV-Vis spectrum B is similar to that expected for " S_{10}^{2+} " or " S_{11}^{2+} ". Thus the spectrum of S_8^{2+} in fluorosulfuric acid shown in Figure 1 is experimentally more reliable than that obtained on oxidation of sulfur by AsF_5 in SO_2 and shown as trace B in Figure 2. In addition to the higher concentration of $\text{S}_8(\text{AsF}_6)_2$ in the experiment with HSO_3F as a solvent, the method passivates the glass surfaces. Some solution was added to the rigorously dried 1.0 cm cell in the dry box, a spacer was slowly inserted into the cell forcing solution over the glass surfaces up above the insert and away from the spectrometer beam. At first the blue solution was seen to decrease in intensity as it passed over the surfaces., but this ceased as more solution moved up the cell (J. Passmore, cf. ref. 11).