Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Figure S1 The detailed view of the applied periodic (left) and cluster models (right) on example of *cis*-$S_4Na_7Cl(Si_6Al_6O_{24})$ model (48 atoms/unit cell). The cluster cut from the periodic structure consists of the whole truncated cubooctahedral SOD cage with S_4 species inside. The dangling O atoms in cluster model are saturated with H atoms, put along the line of broken O—Si/Al bond. The formula of cluster is $(S_4Na_7Si_{12}Al_{12}O_{60}H_{24})^{-5}$. Atom coloration (as used in whole paper): S — yellow, Na – purple, O — red, Si/Al — dark/light blue, H — white (cluster model only), Cl — green.

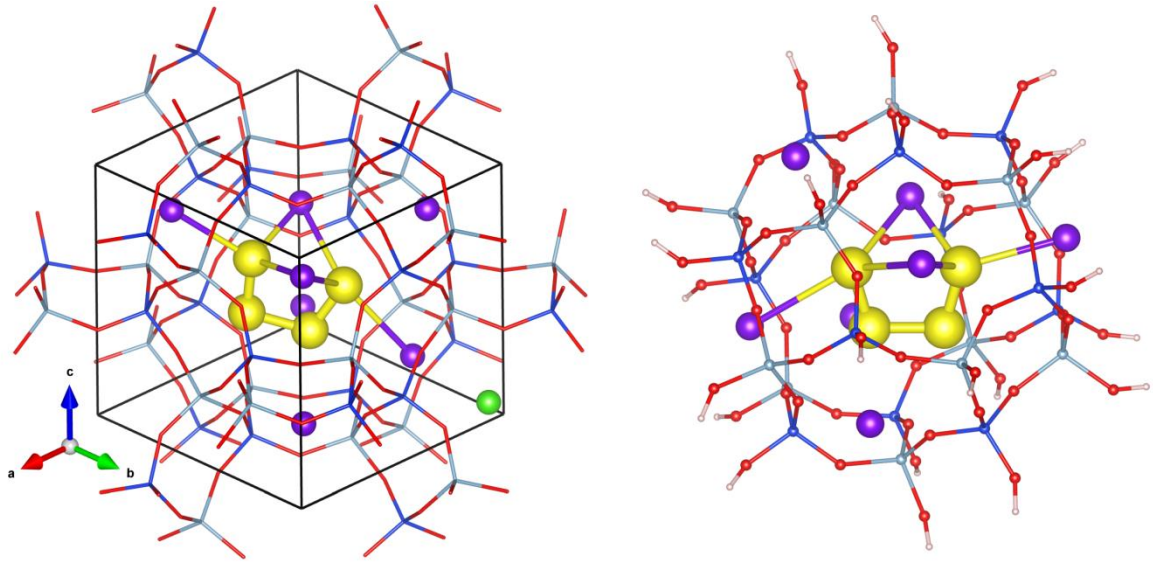


Figure S2 Broken spin symmetry singlet solutions for *cis*–C_{2v} (top) and *trans*–C_{2h} (bottom) isomers of S_4: plots of the highest occupied orbitals for both spin components (left and middle) and spin density (right). Broken spin solutions are of 6 and 16 kJ/mol lower energy than the restricted solutions for *cis* and *trans* isomer, respectively. The values of S^2 are 0.46 and 0.66 for *cis* and *trans* isomer, respectively.

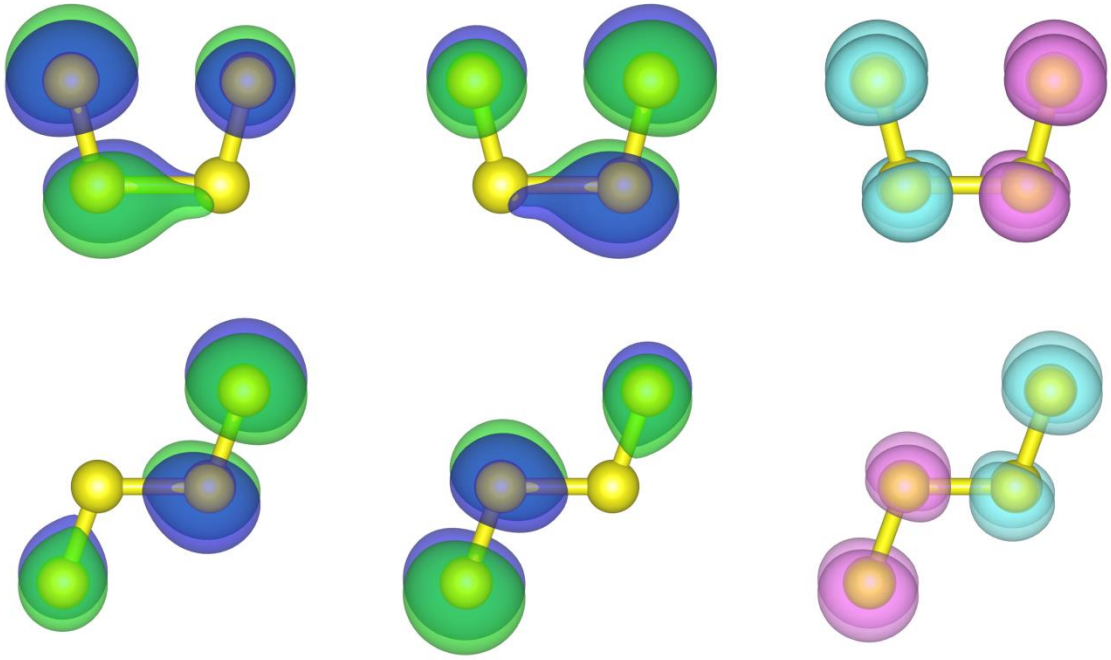


Table S1 DFT/B3LYP results for the isomers of isolated S_4 and $S_4^{\bullet-}$ species: bond lengths (R, in Å), bond angles (Θ, in °) and relative energetic stabililities (ΔE, in kJ/mol). See Figure 1 in main text for atom labeling.

	S_4					
	cis–C_{2v}	*trans*–C_{2h}	D_{2h}	C_s	D_{2d}	D_{3h}
	def2-TZVP/def2-QZVPP					
$R_{S1–S2/S1'}$	1.915/1.917	1.931/1.933	1.897/1.902	1.909/1.911	2.131/2.138	1.914/–
$R_{S2–S2'}$	2.121/2.129	2.079/2.080	2.558/2.543	2.177/2.180		
$\Theta_{122'}$	107.55/107.02	111.31/111.41	90.00	116.35/116.45	85.00/85.08	120.00/–
$R_{S3–S3'}$	–	–	–	2.111/2.114	–	–
ΔE	0	28/27	15/16	57/57	80/80	88/89

	$S_4^{\bullet-}$				
	cis–C_{2v}	*trans*–C_{2h}	D_{2h}	C_{3v}	C_s
	ma-def2-TZVP/ma-def2-QZVPP				
$R_{S1–S2}$	1.978/1.980	2.002/2.001	1.953/1.956	2.001/2.004	1.996/2.000
$R_{S2–S2'}$	2.213/2.216	2.138/2.135	2.692/2.698	–	2.087/2.088
$\Theta_{122'}$	109.55/109.38	108.72/108.75	90.00/90.00	115.87/115.87	113.43/113.11
$R_{S3–S3'}$	–	–	–	–	2.835/2.838
ΔE	3/3	0/0	21/23	71/70	92/92

Table S2 The multireference diagnostics obtained for $S_4/S_4^{\bullet-}$ species: CASSCF natural orbital occupation numbers (NOON), CCSD(T) maximum norm of double amplitudes ($|t_2|_{max}$) and T_1 diagnostics, along with the stability test of unrestricted Kohn-Sham solutions for singlet S_4. NOONs for S_4 HOMO/LUMO and $S_4^{\bullet-}$ SOMO are underlined, the values deviating by more than 0.1 from the single configuration integer occupation depicted in bold. The character of excited configuration corresponding to $|t_2|_{max}$ given in parenthesis.

Isomer	NOON	$\|t_2\|_{max}$	T_1	UKS stability PBE/B3LYP
	S_4			
cis–C_{2v}	1.954, **<u>1.756</u>**, **<u>0.298</u>**, 0.085	0.178 (HOMO → LUMO)	0.023	Y/N
trans–C_{2h}	1.957, **<u>1.692</u>**, **<u>0.354</u>**, 0.070	0.188 (HOMO → LUMO)	0.024	N/N
C_s	1.944, <u>1.943</u>, <u>0.089</u>, 0.066	0.047 (HOMO-5 → LUMO)	0.024	Y/Y
D_{2d}	1.958, 1.958, <u>1.957</u>, <u>0.046</u>, <u>0.046</u>	0.062 (HOMO-3/-4 → LUMO+2)	0.015	Y/Y
D_{3h}	1.965, 1.965, <u>1.944</u>, <u>1.944</u>, **<u>0.126</u>**, 0.043	0.162 (HOMO-1/-2 → LUMO+2)	0.019	Y/Y
	$S_4^{\bullet-}$			
cis–C_{2v}	1.961, 1.940, <u>1.059</u>, 0.095, 0.039	0.052 (SOMO-1 → SOMO, SOMO-2 → SOMO+12)	0.023	-
trans–C_{2h}	1.967, 1.947, <u>1.050</u>, 0.078, 0.036	0.043 (SOMO-1 → SOMO, SOMO-2 → SOMO+12)	0.024	-
D_{2h}	1.933, **1.897**, <u>1.088</u>, **0.180**, 0.027	0.082 (SOMO-1 → SOMO, SOMO-2 → SOMO+5)	0.014	-
C_{3v}	1.963, 1.963, <u>1.029</u>,0.059, 0.038, 0.038	0.022 (SOMO-1 → SOMO+11, SOMO-7 → SOMO)	0.023	-
C_s	1.959, 1.957, <u>1.029</u>, 0.059, 0.056	0.030 (SOMO-1 → SOMO, SOMO-1 → SOMO+15)	0.025	-

Table S3 The DFT/PBE calculated unit cell parameters for $S_4/S_4^{\bullet-}$ hosting sodalite lattices. For comparison also experimental and computed data for pristine sodalite are given.

			S_4Na_8Ssod		
	cis–C_{2v}	*gauche*–C_2[1]	C_s	D_{2d}	D_{3h}
V_{cell} (Å^3)	737.47	757.41	733.51	753.05	749.78
a, *b*, *c* (Å)	9.025, 9.030, 9.050	9.076, 9.091, 9.181	8.999, 8.998, 9.060	9.139, 9.111, 9.044	9.047, 9.039, 9.169
α, β, γ (°)	90.00, 90.00, 90.51	89.53, 88.97, 89.89	90.66, 90.71, 90.07	90.00, 90.00, 90.00	89.46, 90.10, 89.52
			S_4Na_7Clsod		
	cis–C_{2v}	*trans*–C_{2h}	C_s	D_{2d}	D_{3h}
V_{cell} (Å^3)	739.96	764.38	738.69	757.11	762.57
a, *b*, *c* (Å)	9.061, 9.059, 9.016	9.061, 9.089, 9.074	9.006, 9.044, 9.069	9.148, 9.115, 9.080	9.047, 9.039, 9.169
α, β, γ (°)	90.34, 89.66, 90.81	90.86, 89.59, 90.41	89.31, 90.13, 90.11	90.43, 90.30, 89.96	89.46, 90.10, 89.52
			$S_4^{\bullet-}Na_8Cl$–sod		
	cis–C_{2v}–1	*cis*–C_{2v}–2	*gauche*–C_2[a]	C_s	C_{3v}
V_{cell} (Å^3)	760.06	753.91	744.67	742.58	749.22
a, *b*, *c* (Å)	9.100, 9.172, 9.108	9.059, 9.090, 9.156	9.065, 9.050, 9.080	9.032, 9.028, 9.107	9.082, 9.083, 9.083
α, β, γ (°)	89.44, 89.12, 89.36	90.00, 90.00, 90.81	89.95, 88.86, 89.94	89.42, 89.43, 89.98	89.49, 89.49, 90.51
			$S_4^{\bullet-}Na7sod$		
	cis–C_{2v}–1	*cis*–C_{2v}–2	C_{3v}	-	-
V_{cell} (Å^3)	775.39	770.85	778.39		
a, *b*, *c* (Å)	9.226, 9.151, 9.186	9.204, 9.163, 9.141	9.237, 9.243, 9.118		
α, β, γ (°)	90.28, 88.67, 89.95	89.61, 89.18, 89.68	89.60, 89.74, 90.91		
			Sodalite (*P-43n*)		
		Exp.[b]			DFT
V_{cell} (Å^3)		699.05			707.63
a, *b*, *c* (Å)		8.875			8.911
α, β, γ (º)		90.0			90.0

[a]Converged from initial C_{2h} geometry. [b] I. Hassan and H. D. Grundy, *Acta Crystallogr. B*, 1984, **40**, 6–13.

Table S4 The supplement to Table 4 in main text: number of lattice O ions coordinating S atoms (CN) and the range of S-O distance (R, in Å) within 3.40 Å radius. O ions bound to more than one S atoms underlined.

	S_4 models		$S_4^{\bullet-}$ models	
	cis S_4Na_8Ssod	*cis* S_4Na_7Clsod	*cis* $S_4^{\bullet-}Na_8Clsod$	*cis* $S_4^{\bullet-}Na_7sod$
CN_{S1-O}/R_{S1-O}	3/3.196–3.290	1/3.349	2/3.097, 3.343	1/3.269
$CN_{S1'-O}/R_{S1'-O}$	3/3.196–3.290	3/3.169, 3.196, <u>3.299</u>	3/3.250, 3.279, 3.343	2/3.284, 3.390
CN_{S2-O}/R_{S2-O}	3/3.164–3.377	2/3.048, <u>3.182</u>	3/3.298, 3.328, 3.387	3/3.317, 3.332, 3.387
$CN_{S2'-O}/R_{S2'-O}$	3/3.164–3.377	4/2.955, 2.971, <u>3.108</u>, 3.387	2/3.198, 3.346	3/3.304, 3.339, 3.368

Table S5 The DFT/PBE data obtained for S_4 species embedded in periodic models: bond lengths (R, in Å), bond angles and torsions (Θ and ϕ, in °), total numbers of Na ions coordinating S_4 molecule ($CN_{(S4)-Na}$), numbers of Na and O ions coordinating S atoms ($CN_{Sx-Na/O}$) and Bader electronic charges (Q). The coordination distances set to 3.40 Å. $R_{intermol}$ denotes the nearest distance between S_4 species occupying adjacent SOD cages. For atom and bond angles numbering see Figure 1 in main text.

	trans–C_{2h}[a]	*C_s*	*D_{2d}*	*D_{3h}*
		S_4Na_8Ssod		
$R_{S1–S2}$	1.940, 1.980	1.937	2.118, 2.154	1.916, 1.936, 1.945
$R_{S2–S2'/S2–S3, S2–S3'}$	2.076	2.144, 2.148	–	–
$Θ_{122', 1'2'2/123, 123'}$	104.47, 103.99	111.16, 111.20	85.20	120.50, 117.53, 121.90
$R_{S3–S3'}$	–	2.101	–	–
$Θ_{323'}$	–	58.62	–	–
$ϕ_{122'1'/11'1''3}$	134.75	–	32.57	1.706
total $CN_{(S4)–Na}$	5	3	4	4
S_x $CN_{Sx–Na}/R_{Sx–Na}$	S1 1/2.987 S1′ 2/2.979, 2.855 S2 0/– S2′ 2/2.986, 2.973	S1 3/2.956,[b] 3.031, 3.299 S2 0/– S3 1/3.248 S3′ 3.116	1/2.904	S1 0/– S1′ 2/2.867, 3.246 S1′′ 1/2.814 S2 1/3.278
S_x: $CN_{Sx–O}/_{RSx–O}$[3]	S1 5/2.623–3.364 S1′ 5/2.626–3.324 S2, S2′ 0/–	S1 3/3.069–3.267 S2 0/– S3 2/3.018, 3.174 S3′ 3/3.038–3.347	1/3.146	S1 2/2.728, 3.056 S1′ 2/2.729, 3.166 S1′′ 3/2.882–3.399 S2 0/–
$R_{intermol}$	6.338 (S1–S1′)	6.839 (S1–S3′)	7.075	6.122 (S1–S1′)
S_x Q_{Sx}	S1 -0.08, S1′ -0.25 S2 0.03, S2′ -0.16	S1 -0.25, S2 0.24 S3 -0.03, S3′ -0.03	S1-S1‴ -0.03	S1 -0.01, S1′ -0.10, S1′′ -0.01, S3 -0.03
		S_4Na_7Clsod		
$R_{S1–S2}$	1.892, 2.003	1.957	2.123, 2.125, 2.148, 2.154	1.925, 1.933, 1.933
$R_{S2–S2'/S2–S3, S2–S3'}$	2.107	2.133, 2.136	–	–
$Θ_{122', 1'2'2/123, 123'}$	109.26, 103.04	111.45, 115.62	83.51, 86.72, 82.23, 83.64	119.35, 118.82, 121.81
$R_{S3–S3'}$	–	2.106	–	–
$Θ_{323'}$	–	59.10	–	–
$ϕ_{122'1'/11'1''3}$	174.75	–	33.83	178.36
total $CN_{(S4)–Na}$	4	4	4	6
S_x $CN_{Sx–Na}/R_{Sx–Na}$	S1 0/– S1′ 2/2.794, 3.054 S2 1/3.364 S2′ 2/2.836, 2.856	S1 2/2.792, 2.971 S2 1/3.020 S3 2/3.247, 3. 261 S3′ 0/–	S1 1/3.239 S1′ 2/2.808, 3.179 S1′′ 1/3.346 S1‴ 2/2.812, 3.150	S1 1/3.247 S1′ 2/2.824, 3.218 S′′ 1/2.873 S3 1/3.378
S_x $CN_{Sx–O}/_{RSx–O}$[c]	S1 6/2.414–3.350 S1′ 3/2.869–3.312 S2 1/3.212 S2′ 0/–	S1 1/3.159 S2 0/– S3 3/2.834–3.315 S3′ 4/2.602–3.358	S1 0/– S1′ 2/3.162, 3.173 S1′′ 3/2.845–3.382 S1‴ 2/3.181, 3.223	S1 2/2.843, 3.114 S1′ 3/2.724–3.382 S1′′ 2/2.836, 3.188 S3 0/–
$R_{intermol}$	6.951 (S1–S1′)	6.681 (S1–S3)	7.001 (S1–S1‴)	6.576 (S1–S1′)
S_x Q_{Sx}	S1 0.24, S1′ -0.40, S2 -0.06, S2′ -0.16	S1 -0.31, S2 0.12, S3 -0.05, S3′ 0.11	S1 -0.03, S1′ -0.07, S1′′ 0.07, S1‴ -0.08	S1 -0.04, S1′ -0.06, S1′′ -0.03, S2 -0.01

[a]In the case of model converged to *gauche–C_2* like structure (actual symmetry C_1). [b]Underlining depicts the Na ions bound to more than one S atoms. [c]For more than two O atoms in the vicinity of S atoms only the range of S–O distances is given.

Table S6 The DFT/PBE data obtained for $S_4^{\bullet-}$ species embedded in periodic models: bond lengths (R, inÅ), bond angles and torsions (Θ and ϕ, in °), total numbers of Na ions coordinating S_4 molecule ($CN_{(S4)–Na}$), numbers of Na and O ions coordinating S atoms ($CN_{Sx–Na/O}$), Bader electronic (Q) and spin ($N^{\alpha–\beta}$) charges. The coordination distances set to 3.40 Å. $R_{intermol}$ denotes the nearest distance between S_4 species occupying adjacent SOD cages. For atom and bond angles numbering see Figure 1 in main text.

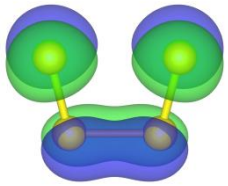
	$(S_4^{\bullet-})Na_8$Clsod			
	cis–C_{2v}–2	*gauche*–C_2	C_s	C_{3v}
$R_{S1–S2}$	1.961, 1.961	2.004, 2.008	1.975	1.973
$R_{S2–S2'/S2–S3, S2–S3'}$	2.232	2.130	2.065, 2.066	–
$Θ_{122', 1'2'2/123, 123'}$	101.72, 101.72	97.58, 96.56	108.99, 109.29	115.00
$R_{S3–S3'}$	–	–	2.766	–
$Θ_{323'}$	–	–	84.06	–
$ϕ_{122'1'/11'1''3}$	2.77	70.79	–	25.00
total $CN_{(S4^{\bullet-})–Na}$	6	6	7	7
S_x $CN_{Sx–Na}/R_{Sx–Na}$	S1 3/2.902,[a] 2.939, 3.031 S2 1/3.013	S1 4/2.989, 3.104, 3.116, 3.299 S1′ 3/2.941, 3.020, 3.132 S2 2/2.741, 3.021 S2′ 2/2.742, 2.997	S1 4/2.925, 2.926, 3.268, 3.386 S2 2/3.073, 3.076 S3 4/2.896, 3.028, 3.255, 3.314 S3′ 4/2.893, 3.043, 3.255, 3.307	S1 3/2.873, 2.900, 3.187 S2 1/2.901
S_x: $CN_{Sx–O}/R_{Sx–O}$[b]	S1 3/3.185–3.363 S2 1/3.251	S1 3/3.095–3.158 S1′ 3/2.998–3.173 S2 1/3.397 S2′ 2/3.284, 3.395	S1 2/3.074, 3.086 S2 0/– S3 3/3.111, 3.265, 3.314 S3 3/3.115, 3.231, 3.277	S1 3/3.090, 3.138, 3.375 S2 0/–
$R_{intermol}$	7.058 (S1–S1′)	6.871 (S1–S1′)	6.817 (S1–S3′)	7.100 (S1–S1)
S_x $Q_{Sx}/N^{\alpha-\beta}{}_{Sx}$	S1 -0.36/0.21 S2 -0.06/0.27	S1, S1′ -0.11/0.35 S2, S2′ -0.33/0.15	S1 -0.40/0.00 S2 0.11/0.00 S3, S3′ -0.30/0.48	S1 -0.31/0.24 S2 0.05/0.22

	$(S_4^{\bullet-})Na_7$sod	
	cis–C_{2v}–2	C_{3v}
$R_{S1–S2}$	1.940, 1.980	1.964, 1.994, 1.995
$R_{S2–S2'/S2–S3, S2–S3'}$	2.254	–
$Θ_{122', 1'2'2/123, 123'}$	100.01, 102.03	115.72, 109.37, 116.09
$ϕ_{122'1'/11'1''3}$	3.89	26.00
total $CN_{(S4^{\bullet-})-Na}$	6	6
S_x CN_{Sx-Na}/R_{Sx-Na}	S1 2/2.826, 2.829 S1′ 3/2.832, 2.945, 3.076 S2 0/- S2′ 3/2.762,3.168, 3.213	S1 1/3.214 S1′ 3/2.903, 2.906, 2.929 S1′′ 3/2.844, 2.917, 3.048 S3 1/3.245
S_x $CN_{Sx-O}/\{R_{Sx-O}\}^{Y}$	S1 5/3.055-3.399, S1′ 2/3.293, 3.338 S2 3/3.233-288, S2′ 1/3.342	S1 3/3.080-3.350, S1′ 5/3.186-3.385 S1′′ 2/3.069, 3.250, S3 0/-
$R_{intermol}$	6.520 (S1-S2′)	6.462 (S1-S1′′)
S_x $Q_{Sx}/N^{\alpha-\beta}{}_{Sx}$	S1 -0.31/0.30 S1′ -0.40/0.16 S2 0.04/0.33 S2′ -0.20/0.18	S1 -0.17/0.33, S1, S1′′ -0.40/0.19 S2 0.06/0.22

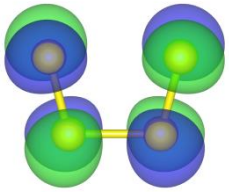
[a]Underlining depicts the Na^+ ions bound to more than one S atoms. [b]For more than two O atoms in the vicinity of S atoms only the range of S - O distances is given.

Figure S3 DFT frontier orbitals for gas phase S_4 isomers.

cis–C$_{2v}$

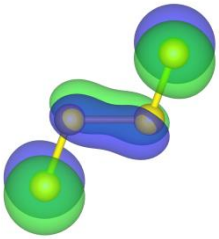


4b$_1$ HOMO

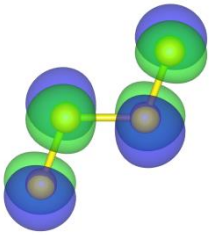


4a$_2$ LUMO

trans–C$_{2h}$

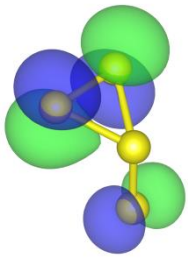


4a$_u$ HOMO

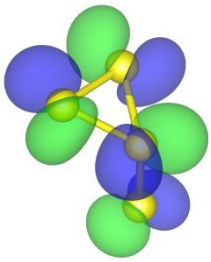


4b$_g$ LUMO

C$_s$

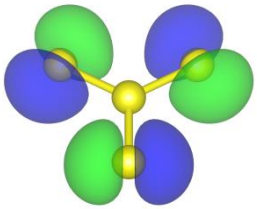


11a′ HOMO

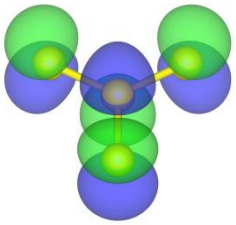


12a′ LUMO

D$_{3h}$

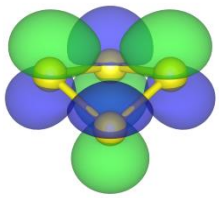


2a$_2$′ HOMO

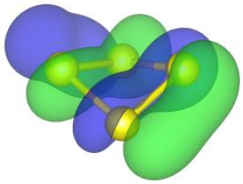


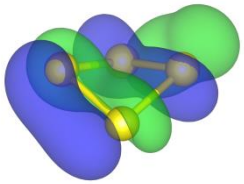
4a$_2$″ LUMO

D$_{2d}$



7a$_1$ HOMO

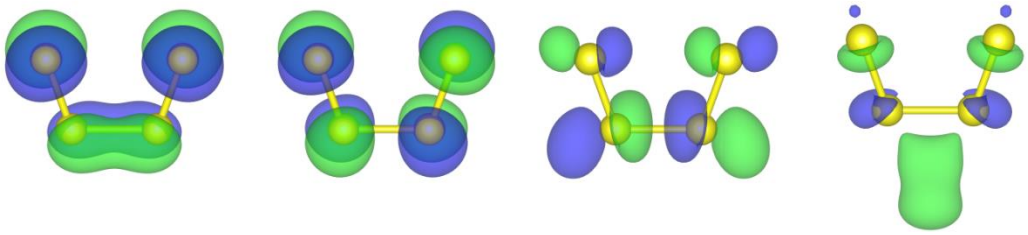




9e LUMO

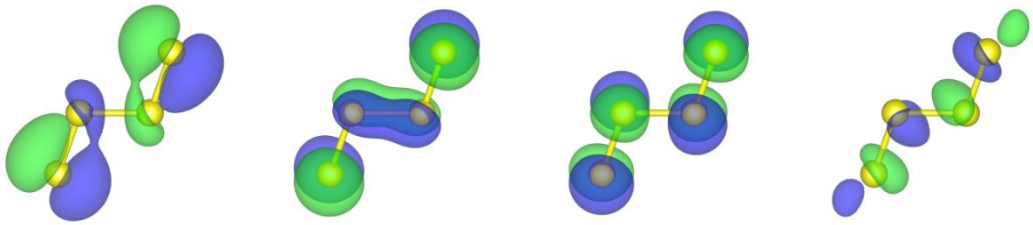
Figure S4 The most relevant for optical transitions (see Table 7 in main text) MOs of gas phase $S_4^{\bullet-}$ radical.

cis–C_{2v}



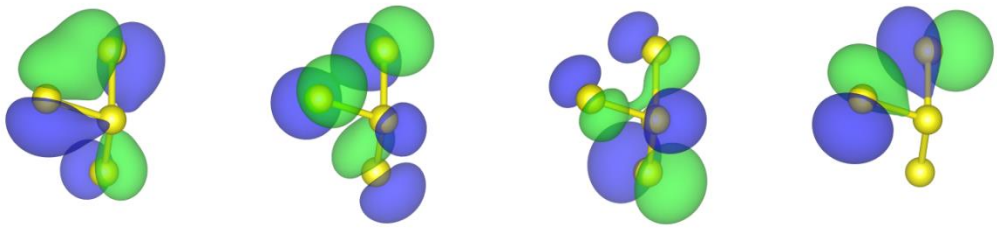
SOMO-1 $4b_1$ SOMO $4a_2$ SOMO+1_α $13b_2$ SOMO+1_β $14a_1$

trans–C_{2h}



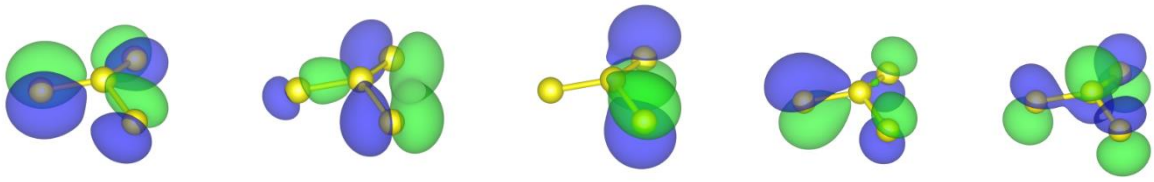
SOMO-3 $12b_u$ SOMO-1 $4a_u$ SOMO $4b_g$ SOMO+1 $13b_u$

C_s



SOMO-5 *19a′* SOMO-3 *20a′* SOMO-1 *21a′* SOMO *12a″*

C_{3v}



SOMO-3 *9e* SOMO-2 *10e* SOMO $11a_1$

Table S7 TDDFT/LC-BLYP electronic transitions within the range of 350-800 nm for S_4 chromophores embedded in SOD cages: wavelengths λ and oscillator strengths f_{osc} (in parenthesis), along with the dominant orbital contribution are given. The S_4 isomers and the relevant orbitals are labeled according to the ideal symmetry of the corresponding gas phase S_4 species (compare with Table 6 in manuscript), even if the actual symmetry of embedded is lower.

S_4 isomer	λ (nm), f_{osc}	TDDFT excitation character
		$(S_4)Na_8Ssod$
cis–C_{2v}	507 (0.120)	$4b_1$ /HOMO/ $\rightarrow$ $4a_2$ /LUMO/ (76%)
		$13a_1$ /HOMO-2/ $\rightarrow$ $13b_2$ /LUMO+1/ (22%)
gauche–C_2 (C_1)[a,b]	704 (0.179)	*17a* /HOMO/ $\rightarrow$ *4b* /LUMO/ (66%)[c]
		16a /HOMO-1/ $\rightarrow$ *16b* /LUMO+1/ (10%)[c]
	371 (0.044)	O *2p* $\rightarrow$ $4b_g$ /LUMO/[d]
C_s	475 (0.002)	*11a''* /HOMO/ $\rightarrow$ *12a''* /$LUMO/_{S4}$ (74%)[e]
		10a'' /HOMO-2/ $\rightarrow$ *12a''* /$LUMO/_{S4}$ (17%)
	361 (0.003)	*21a'* /HOMO-1/ $\rightarrow$ *12a''* /$LUMO/_{S4}$ (85%)
D_{2d} (D_2)	591 (0.002)	$7a_1$ /HOMO/ $\rightarrow$ *9e*(1) /LUMO/ (92%)[f]
	517 (0.002)	$7a_1$ /HOMO/ $\rightarrow$ *9e*(2)/LUMO+1/4 (92%)[f]
D_{3h} (C_1)	356 (0.158)	*2e'* (+ O *2p*) /HOMO-1/ $\rightarrow$ $4a_2''$ /LUMO/ (>60%)[g]
	352 (0.166)	
		$(S_4)Na_7Clsod$
cis–C_{2v}	478 (0.147)	$4b_1$ /HOMO/ $\rightarrow$ $4a_2$ /LUMO/ (83%)
trans–C_{2h} (C_1)	612 (0.072)	$\pi^*_{S1'-S2'}$ /HOMO/ $\rightarrow$ π^*_{S1-S2} /$LUMO/_{S4}$ (78%)[h]
	393 (0.006)	$12b_u$ (+ O *2p*) /HOMO-2/ $\rightarrow$ π^*_{S1-S2} /$LUMO/_{S4}$ (36%)
		$13a_g$ /HOMO-1/ $\rightarrow$ π^*_{S1-S2} /$LUMO/_{S4}$ (35%)
C_s	502 (0.003)	*11a''* /HOMO/ $\rightarrow$ *12a''* /$LUMO/_{S4}$ (74%)
D_{2d} (C_1)	509 (0.002)	$7a_1$ /HOMO/ $\rightarrow$ $9a_2$ /$LUMO/_{S4}$ (44%)[f]
		$7a_1$ /HOMO/ $\rightarrow$ *9e*(1) /$LUMO+1/_{S4}$ (37%)[f]
	482 (0.003)	$7a_1$ /HOMO/ $\rightarrow$ *9e*(2) /$LUMO+2/_{S4}$ (64%)
		$7a_1$ /HOMO/ $\rightarrow$ *9e*(1) /$LUMO+1/_{S4}$ (16%)
D_{3h}	359 (0.159)	*2e'* /HOMO/ $\rightarrow$ $4a_2''$ /$LUMO/_{S4}$ (31%)
		O *2p* $\rightarrow$ $4a_2''$ /$LUMO/_{S4}$ (>36%)

[a]Converged from initial C_{2h} geometry. [b]The actual symmetry of embedded molecule in parenthesis. [c]Within twisted *gauche*–C_2 geometry orbitals *16a*, *17a* (HOMO) and *16b* (LUMO) correspond to $13a_g$, $4a_u$ and $4b_g$ orbitals, respectively, of the planar C_{2h} isomer. [d]Charge transfer between lattice O *2p* states and LUMO localized at S_4, see Figure S5. [e]$LUMO_{S4}$ denotes LUMO localized predominantly at S_4 molecule, in cases when there are lower lying empty orbitals localized at cluster terminating OH groups and Na^+ ions (likely artefact of cluster model). [f]Upon lowering symmetry from D_{2d} to D_2, $7a_1$ orbital should be relabeled as *9a*, whereas *9e* split into $9b_2$ (LUMO) and $9b_1$ (LUMO+1). [g]Notable admixture of O *2p* lattice states to S_4 localized part, see Figure S6. [h]See Figure S7 below for the explanation of π^* notation.

Figure S5 Differential electron density for the excitation at 371 nm for C_2-(S_4)Na_8Ssod model: electron inflow in cyan, outflow in pink.

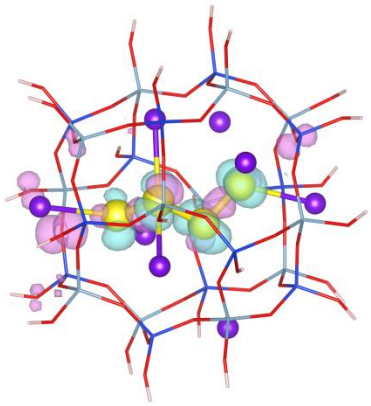


Figure S6 HOMO-1 for D_{3h}-(S_4)Na_8Ssod model, see notable mixing of O *2p* lattice states and S_4 localized part of the orbital.

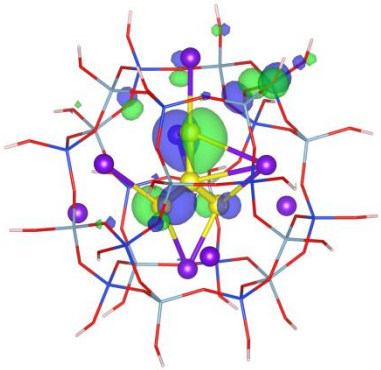


Figure S7 Frontier orbitals in cluster models cut from *trans*-(S_4)Na_7Clsod model: HOMO (left) and $LUMO_{S4}$ (right, i. e. the lowest empty orbital localized primarily on S_4 moiety). Unlike in the ideal C_{2h} symmetry gas phase *trans*-S_4: here HOMO is localized mainly at the longer terminal bond (S1'-S2' atoms), whereas $LUMO_{S4}$ is localized at shorter bond (S1-S2 atoms), both orbitals are π^* type.

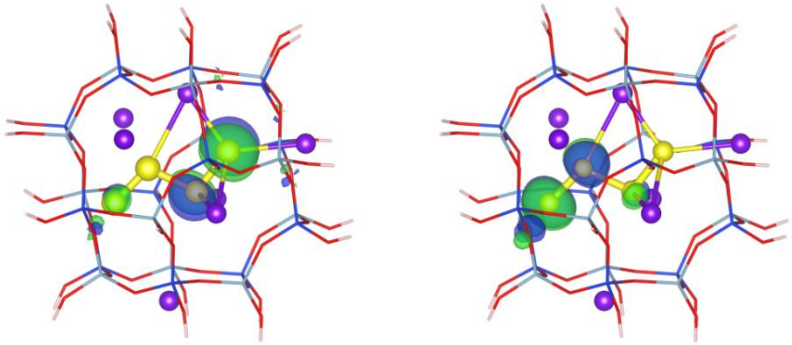
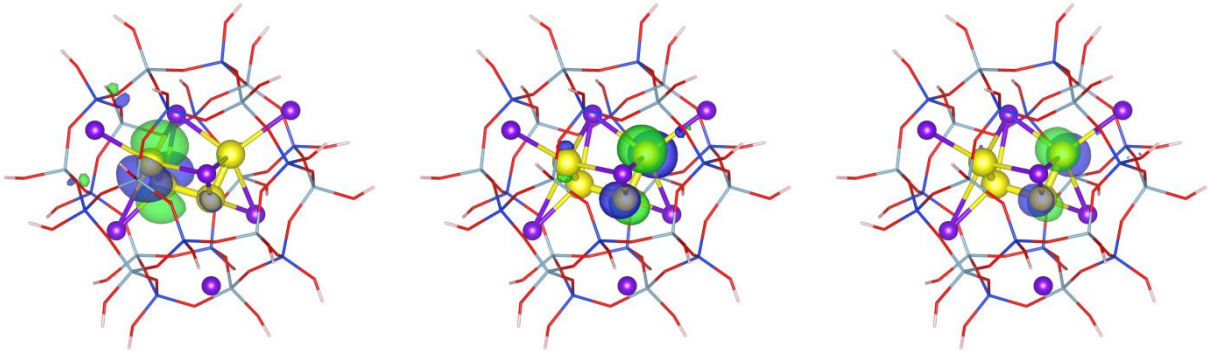


Table S8 Selected TDDFT/LC-BLYP electronic transitions within the range of 350-900 nm for $S_4^{\bullet-}$ chromophores embedded in SOD cages: wavelengths λ and oscillator strengths f_{osc} (in parenthesis), along with the dominant orbital contribution are given. Note that $S_4^{\bullet-}$ isomers and the relevant orbitals are labeled according to the ideal gas phase symmetry of the corresponding $S_4^{\bullet-}$ species (compare with Table 7 in manuscript), the actual symmetry of embedded species is often lower. All transitions within minority spin channel, unless specified otherwise (α subscript).

S_4 isomer	λ (nm), f_{osc}	Excitation character
		$(S_4^{\bullet-})Na_8Clsod$
cis-C_{2v}–*1* (C_1)[a]	775 (0.034)	$4b_1$ /SOMO-1/ $\rightarrow$ $4a_2$ /SOMO/ (82%)
	715 (0.006)	$13a_1$ /SOMO-2/ $\rightarrow$ $4a_2$ /SOMO/ (75%)
		$12b_2$ /SOMO-1/ $\rightarrow$ $4a_2$ /SOMO/ (11%)
	359 (0.015)	$3a_2$ (+O *2p*) /SOMO-7, -8/ $\rightarrow$ $4a_2$ /SOMO/ (50%)
cis–C_{2v}–2	890 (0.046)	$4b_1$ /SOMO-1/ $\rightarrow$ $4a_2$ /SOMO/ (91%)
	376 (0.012)	$3a_2$ (+O *2p*) /SOMO-3/ $\rightarrow$ $4a_2$ /SOMO/ (50%)
		$13a_1$ /SOMO-4/$_{S4}$ $\rightarrow$ $4a_2$ /SOMO/ (17%)
gauche-C_2 (C_1)[b]	758 (0.003)	$\pi^*_{S1'\text{-}S2'}$ /SOMO-1/ $\rightarrow$ $\pi^*_{S1\text{-}S2}$ /SOMO+3,+4/ (67%)[c]
	365 (0.015)	$(3p)_{S1',\,S2'} \rightarrow (3p)_{S1}$[d]
C_s	730 (0.008)	*20a'* /SOMO-3/ $\rightarrow$ *12a''* /SOMO/ (62%)
		21a' /SOMO-1/ $\rightarrow$ *12a''* /SOMO/ (30%)
	579 (0.011)	*21a'* /SOMO-1/ $\rightarrow$ *12a''* /SOMO/ (55%)
		20a' /SOMO-3/ $\rightarrow$ *12a''* /SOMO/ (24%)
	403 (0.055)	*19a*' /SOMO-5/ $\rightarrow$ *12a''* /SOMO/ (59%)
		21a' /SOMO-1/ $\rightarrow$ *12a''* /SOMO/ (10%)
C_{3v}	714 (0.058)	*10e* /SOMO-1/ $\rightarrow$ $11a_1$ /SOMO/ (89%)
	494 (0.030)	*9e* /SOMO-2/ $\rightarrow$ $11a_1$ /SOMO/ (74%)
		$(S_4^{\bullet-})Na_7sod$
cis–C_{2v}–1	795 (0.058)	$4b_1$ /SOMO-1/ $\rightarrow$ $4a_2$ /SOMO/ (92%)
	352 (0.022)	$3a_2$ (+O *2p*) /SOMO-3/ $\rightarrow$ $4a_2$ /SOMO/ (>45%)
cis–C_{2v}–2 (C_1)[1]	669 (0.034)	$4b_1$ /SOMO-1/ $\rightarrow$ $4a_2$ /SOMO/$_{S4}$ (91%)
	369 (0.012)	$3a_2$ (+ O *2p*) /SOMO-4, -5/ $\rightarrow$ $4a_2$ /SOMO/ (44%)
		$12b_2$ /SOMO-1/$_\alpha$ $\rightarrow$ $13b_2$ /SOMO+9/$_\alpha$ (21%)
C_{3v} (C_1)[1]	755 (0.037)	*10e*(*a'*) /SOMO-1/ $\rightarrow$ $11a_1$ /SOMO/ (89%)[e]
	487 (0.023)	*9e*(*a''*) (+ O *2p*) /SOMO-7, -10/ $\rightarrow$ $11a_1$ /SOMO/ (56%)[e]
		10e(*a''*) /SOMO-2/ $\rightarrow$ $11a_1$ /SOMO/ (21%)[5]
	437 (0.015)	*9e*(*a'*) (+ O *2p*) /SOMO-12,-13,-14/ $\rightarrow$ $11a_1$ /SOMO/ (75%)[e]

[a]The actual symmetry of embedded $S_4^{\bullet-}$ radical in parenthesis. [b]Converged from initial C_{2h} geometry.[c]See Figure S8, for the explanation of π^* notation. [d]Transition involving multiple pairs of MO, hence difficult for analysis in terms of MO, see excitation difference density in Figure S9 below. [e]*a'*/*a''* in parenthesis denotes the components of *e* orbitals (within ideal C_{3v} symmetry) which are symmetrical/antisymmetrical with respect to vertical mirror plane.

Figure S8 Orbitals participating in 758 nm excitation in *gauche*–C_2–($S_4^{\bullet-}$)Na_8Clsod model: SOMO, localized mainly at the longer terminal bond (S1'–S2'), along with SOMO+3 and SOMO+4, localized at the shorter terminal bond (S1–S2), all orbitals are of π^* type.



SOMO SOMO+3 SOMO+4

Figure S9 Differential electron density for the excitation at 365 nm in *gauche*–C_2–(S_4)Na_8Clsod model: electron inflow in cyan, outflow in pink.

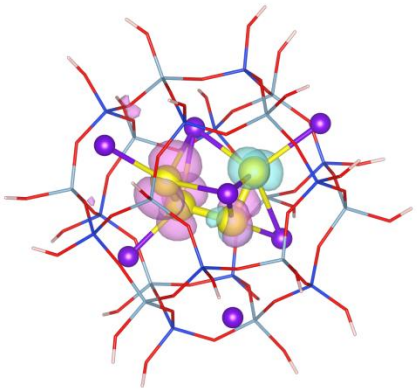
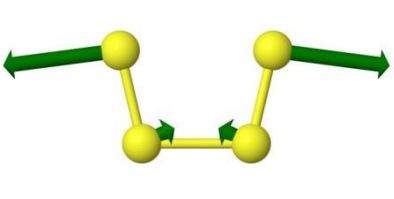


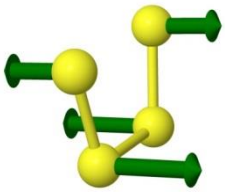
Figure S10 Normal modes for gas phase S_4 molecules at DFT level. The frequencies (in cm^{-1}) are given as (i)/(ii)/(iii), where (i) PBE in def2-TZVP basis set (ORCA), (ii) PBE in PW with E_{cutoff}=40 Ry (Quantum Espresso), and (iii) B3LYP in def2-TZVP basis set (ORCA).

cis–C_{2v}

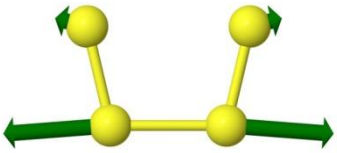
all Raman active



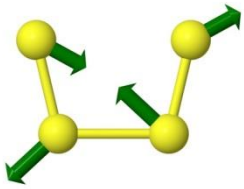
a_1 94/145/107



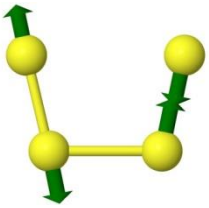
a_2 219/240/212



a_1 319/334/333



b_1 326/339/362



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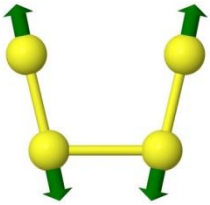
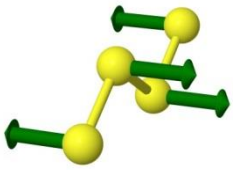


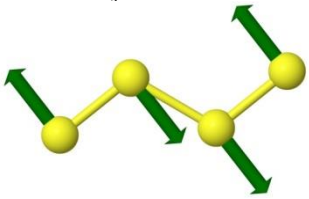
a_1 684/688/671

trans–C_{2h}

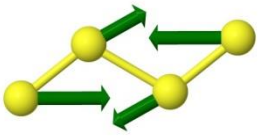
a_g Raman active



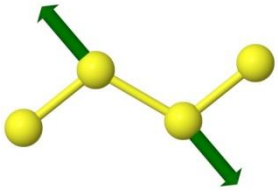
a_u 91/135/94



b_u 109/150/125



a_g 209/227/224



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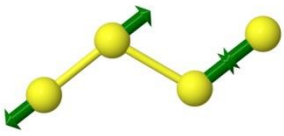
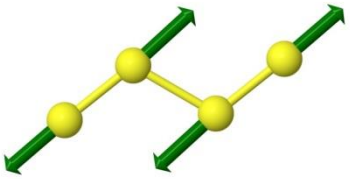


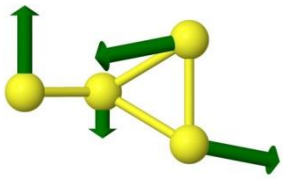
b_u 640/639/630



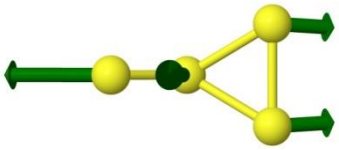
a_g 647/647/644

C_s

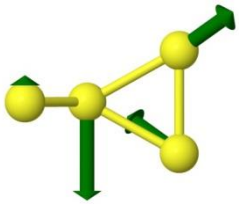
all Raman active



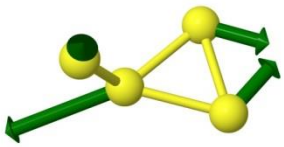
a'' 163/175/166



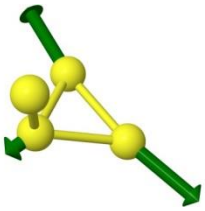
a' 210/220/217



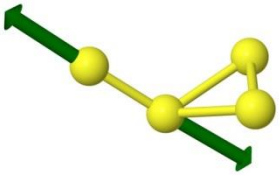
a'' 303/311/306



a' 387/393/386



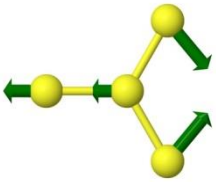
a' 535/544/531



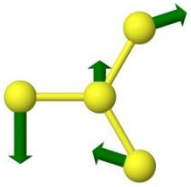
a' 671/670/661

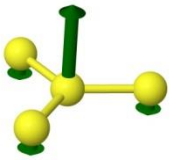
D_{3h}

a_1' and *e'* Raman active

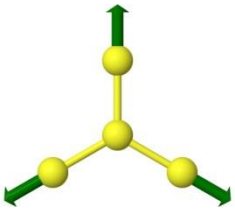


e' 234/237/242

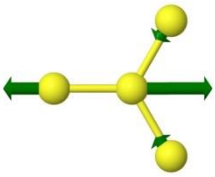




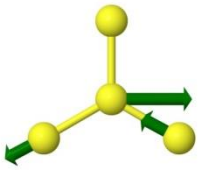
a_2'' 261/258/267



a_1' 466/463/469

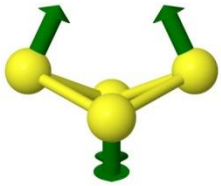


e' 701/697/702

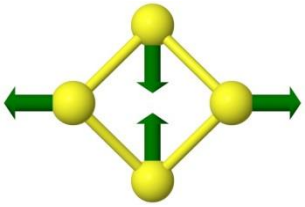


D_{2d}

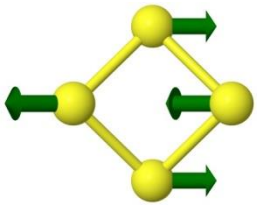
all Raman active



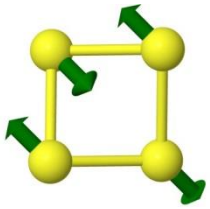
a_1 204/233/199

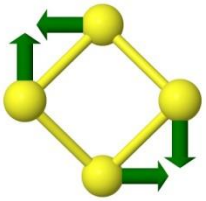


b_2 277/285/299

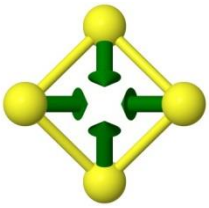


e 399/424/413





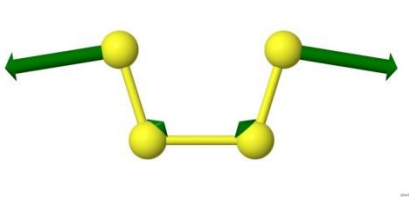
b_1 425/423/440



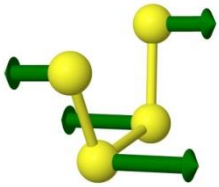
a_1 506/495/504

Figure S11 Normal modes for gas phase $S_4^{\bullet-}$ radicals at DFT level. The frequencies (in cm^{-1}) are given as (i)/(ii)/(iii), where (i) PBE in ma-def2-TZVP basis set (ORCA), (ii) PBE in PW with E_{cutoff}=40 Ry (Quantum Espresso), and (iii) B3LYP in ma-def2-TZVP basis set (ORCA).

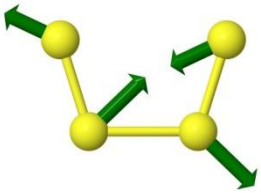
cis–C_{2v}
all Raman active



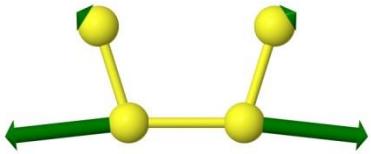
a_1 75/138/91



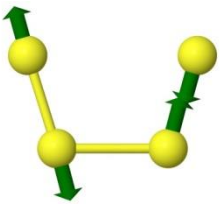
a_2 117/149/105



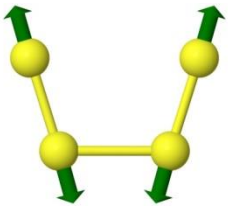
b_1 277/286/282



a_1 284/296/307

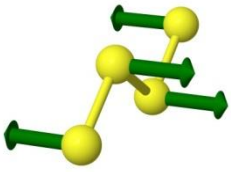


b_1 583/587/563

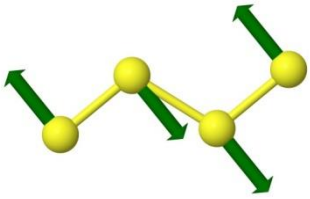


a_1 609/610/591

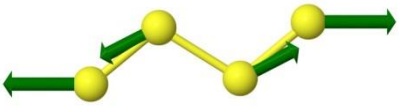
trans–C_{2h}
a_g Raman active



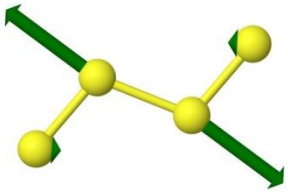
a_u 52/132/59



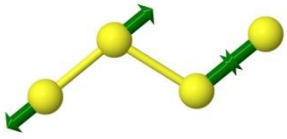
b_u 100/134/114



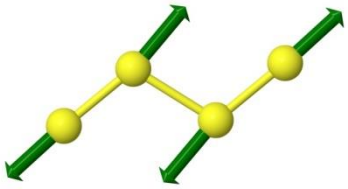
a_g 183/180/195



a_g 414/416/433

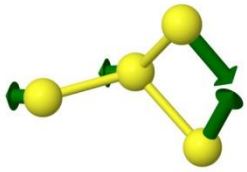


b_u 560/556/537

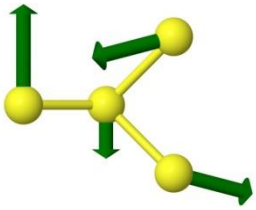


a_g 574/574/564

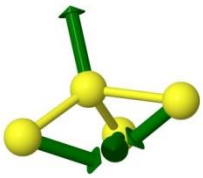
C_s
all Raman active



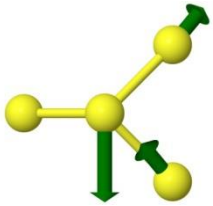
a′ 157/185/172



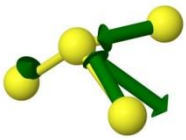
a″ 163/196/173



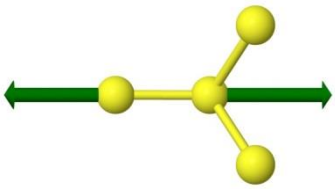
a′ 241/241/248



a″ 400/417/406

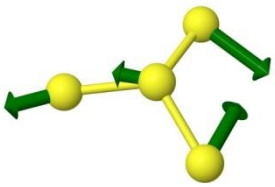


a′ 462/483/467

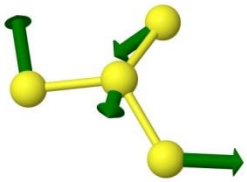


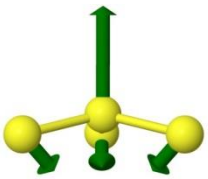
a″ 545/547/534

C_{3v}
all Raman active

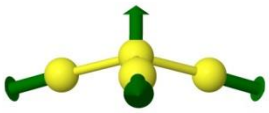


e 200/201/207

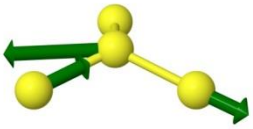


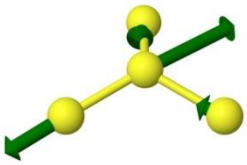


a_1 252/251/251



a_1 418/417/418





e 554/557/550