ON THE ELECTRONIC STATES OF S_4^+ AND S_4^- ISOMERS

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Dedicated to the memory of Professor Jaroslav Koutecký.

For three energetically most stable structures of tetrasulfur, S_4, S_4^+ and S_4^- (*cis*-chain, rectangular, and *trans*-chain forms), equilibrium geometries, harmonic wavenumbers, ionization energies, electron affinities, electronic vertical and adiabatic excitation energies, and electronic transition moments were calculated by ab initio methods. It was found that similarly to the ground state of S_4, the S_4^+ *cis*-isomer could interconvert, perturbed, however, by vibronic coupling with a very close-lying excited state and large-amplitude vibrations. Moreover, the *cis*- and rectangular minima are calculated to be energetically degenerated. The ω values in all three species agree reasonably well with existing experimental and theoretical data. The calculated patterns of harmonic modes suggest the existence of very complex low-lying anharmonic polyads in all three species. The calculated ionization energies reported previously are compared with the present more accurate data. Also the electronic transition moments and the energy positions of the electronic states with higher spin multiplicities are given.
Keywords: Sulfur; Ab initio calculations; Geometry optimization; IR spectroscopy; Ionization potential; Electron affinity.

The allotropic forms of tetrasulfur have been investigated experimentally in the solid and gas phase by various techniques, such as X-ray diffraction, mass, photoelectron, UV, IR, Raman[1–13] and Fourier transform microwave[14,15] spectroscopies. The S_4 appearance ionization energy was reported but no other spectroscopic data for the cationic or anionic forms are known. In crystalline salts the doubly charged species S_4^{2+} and S_4^{2-} were de-

tected by the X-ray diffraction techniques. In cold matrices and in the photoelectron spectrum of S_4^-, several IR transitions were attributed to S_4. The molecular S_4 species show two electronic transitions in visible UV. Photolysis of the green form leads to the red form, and vice versa. Very recently, the experimental gas phase structure of S_4 was determined in a supersonic molecular beam in the centimeter-wave band by Fourier transform microwave spectroscopy. Interestingly, the C_{2v} chain structure shows an interchange tunneling because of the automerization through a transition state with D_{2h} symmetry. The reported rotational transitions of S_4 are of considerable interest for its possible detection in the outer space.

For sulfur clusters a large number of theoretical papers appeared[16–30]. The determination of the most stable neutral isomer has been the subject of controversy for some time. The most recent works assign the global minimum to the singlet *cis*-planar isomer, with the exception of some calculations based on MP2 [19], MP4 [19] or density functional theory[16,29], which predict a singlet rectangular ring as the most stable structure. The next stable isomer of comparable energy is a *trans*-planar chain (C_{2h}), while isomers of higher energy include a branched three-membered ring (C_s), a puckered four-membered ring (D_{2d}) and a planar branched chain (D_{3h}). High-level ab initio calculations[18,21,30] have shown that the rectangular ring is most likely a transition state for the interchange tunneling between two planar equivalent minima of C_{2v} symmetry. The interconversion barrier is calculated to be of around 1 kcal/mol, leading to high tunneling frequencies and detectable splittings of the ro-vibrational levels. The most accurate calculations of the equilibrium structure of the *cis*-planar chain have been done at the CCSD(T)/cc-pVTZ level of theory[15]. The results compare favorably with the empirical equilibrium structure that was obtained by correcting the experimentally determined structure[14] (R_0) with the theoretically calculated vibration-rotation constants[15]. Harmonic vibrational frequencies were reported for the fundamental transitions of the most stable neutral isomers[18,19,22,25,30]. Less theoretical data is available for the charged species[18,20–23,27,28]. Again, as in the neutral case, the three lowest-lying S_4^- and S_4^+ isomers are the *cis*- and *trans*-planar chains, and the rectangular dimer, which was found, by means of single reference calculations[21], to be an unstable stationary point on the adiabatic potential energy surface of both ionic species. Optimized structures for various S_4^+ isomers[21,28] and adiabatic ionization energies[21] were reported as well.

In the present work optimized geometries and harmonic vibrational frequencies for the lowest-lying isomers of neutral, anionic and cationic tetrasulfur are calculated by different ab initio methods with extensive basis

sets. Vertical electronic excitation energies and transition moments are also evaluated by means of time-independent and time-dependent approaches. The results are discussed and compared with the available experimental information and previous theoretical works.

COMPUTATIONAL

For the geometry optimization either the complete active space self-consistent-field method[31] (CASSCF) and Dunning's correlation-consistent basis set cc-pVTZ [32], or the closed-shell coupled-cluster theory in the singles and doubles approximation with perturbative triple excitation corrections[33–35] (CCSD(T)) with the cc-pVQZ [32] basis set were used. For the ionic species the methods used were the CASSCF/cc-pVTZ and the partially spin-restricted open-shell coupled-cluster theory[36] (RHF-RCCSD(T)) with the cc-pVQZ basis set. At the RCCSD(T)/cc-pVTZ level of theory, harmonic vibrational frequencies were calculated for the electronic ground states. In all calculations at the CASSCF level, an active space of 16 orbitals corresponding to the full-valence CAS was employed. The state-averaged (SA) CASSCF method[37] and the time-dependent density functional (TD-DF) approach[38–42], with the B3LYP functional and the 6-311+G(3df) basis set[43], were applied to obtain the relative energies and transition moments of the low-lying electronically excited states of the neutral and ionic isomers. Some of the low-lying singlet vertical transition energies were calculated also by the equation-of-motion coupled-cluster method[44–46] (EOM-CC) with cc-pVQZ basis set. For the TD-DFT calculations, the Gaussian quantum chemistry package[47] was used. All the other calculations have been performed with the MOLPRO quantum chemistry package[48].

RESULTS AND DISCUSSION

The aim of the present work was to provide new theoretical information on the ionic species S_4^+ and S_4^-. In order to get an estimate about the accuracy of the calculated properties of the ions, some calculations have been done also for the neutral tetrasulfur and compared with the most recent experimental and theoretical studies. In Table I the R_e CCSD(T) structure is compared with the empirical R_e structure of Thorwirth et al.[15] based on experimental R_0 structure of McCarthy et al.[14] Both equilibrium geometries agree quite well and are more accurate than previous theoretical data. Our geometries for the ionic species calculated using the same approach should exhibit similar accuracy. Our barrier to the D_{2h} transition state (cf. Table I)

is about 100 cm^{-1} higher than the value in ref.[14] (Fig. 3). This barrier height plays an essential role in the observed automerization of the *cis*-isomer. The infrared spectrum of tetrasulfur was measured in an experiment where the S$_4$ clusters were produced from a microwave discharge of sulfur vapor in argon stream[6]. The two observed absorption bands at 662 and 642 cm^{-1} originate from different isomers, as it was shown by photolysis irradiation. Our calculated harmonic wavenumbers given in Table I are close to the observed transitions, but their assignment to a specific isomer is uncertain. An inspection of the harmonic patterns strongly suggests the presence of anharmonic polyads particularly for the a$_1$ and b$_2$ modes in the *cis*-structure and the a$_g$ and b$_u$ modes in the *trans*-structure. The interconversion nuclear motion dynamics between various tetrasulfur structures will be very complex. Using an external electric field and CCSD(T) energies we have calcu-

TABLE I
Optimized geometries and harmonic wavenumbers of the three lowest-lying isomers of S$_4$. Bond lengths are in atomic units and angles in degrees

Method		C_{2v} (I)			D_{2h} (II)			C_{2h} (III)		
		R_1	R_2	α	R_1	R_2	R_1	R_2	α	
a		3.612	4.070	104.2	3.588	4.819	3.648	3.936	109.6	
b		3.632	4.019	107.0	3.598	4.751	3.664	3.934	109.9	
c		3.630	3.936	107.4	3.581	4.838	3.662	3855	110.0	
Exp^d		3.588	4.073	104.2						
ΔE^a, eV			0.0000			0.0803			0.3890	
		a	b		a	b	a	b		
Modes, cm^{-1}	ω_1	690	674 (a$_1$)		728	724 (a$_g$)	656	649 (a$_g$)		
	ω_2	337	373 (a$_1$)		284	284 (a$_g$)	450	472 (a$_g$)		
	ω_3	122	104 (a$_1$)		336	334 (b$_{3g}$)	224	225 (a$_g$)		
	ω_4	215	207 (a$_2$)		239	245 (a$_u$)	83	93 (a$_u$)		
	ω_5	652	649 (b$_2$)		491	671 (b$_{1u}$)	624	637 (b$_u$)		
	ω_6	329	329 (b$_2$)		i84	i145 (b$_{2u}$)	119	124 (b$_u$)		

^{a} CCSD(T)/cc-pVQZ. ^{b} B3LYP/6-31G(2df); see ref.[30] ^{c} QCISD/cc-pVTZ; see ref.[30] ^{d} Empirical equilibrium structure as described in ref.[15]

lated for the equilibrium structures (cf. Fig. 1) of the neutral and ionic tetrasulfur the dipole moments for the *cis*-forms to be: 1.139 for S_4, 0.157 for S_4^+ and 2.002 for S_4^- (all values in D, for the ions at the center of mass of ^{32}S isotopomer). McCarthy et al. reported 1.15 D for the neutral species. It has been known[14] that the molecular properties of S_4 are extremely sensitive to the sophistication of the theoretical methods employed, and high levels of electron correlation are needed to achieve accurate results.

In Table II the SA-CASSCF singlet vertical electronic transition energies and the electronic transition moments for the *cis*- and *trans*-forms and for the D_{2h} transition state are given. The $X^1A_1 \rightarrow C^1B_2$ transition is calculated to be the strongest of the *cis*-form. An energetically lower and stronger transition $C^1B_u \rightarrow X^1A_g$ exists in the *trans*-form. The electronic absorption bands at 530 nm (2.34 eV) and 620 nm (2.00 eV) were first assigned to S_4 by Meyer et al.[7] Hassanzadeh and Andrews[6] found two distinct electronic transitions of S_4 in the argon matrix. A broad green band was centered at 518 nm and a structured red band between 560 and 660 nm. The red-absorbing species is converted to the green-absorbing species by irradiation with red light and vice versa. This strongly indicates the presence of two distinct isomers. Wong and Steudel[30] used a simple CIS method and assigned the green form to the *cis*-isomer and the *trans*-form to the red S_4. Using the cc-pVQZ basis set and EOM method we have recalculated the SA-CASSCF vertical transition energies and obtained for the $^1B_2$ state 2.609
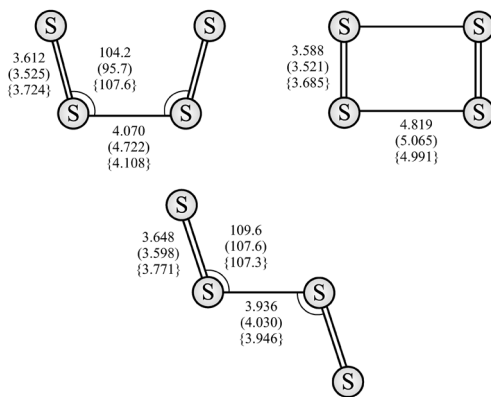

FIG. 1

Optimized geometries of the *cis*-, rectangular and *trans*-isomers of S_4, S_4^+ (round brackets) and S_4^- (curly brackets). CCSD(T) and RCCSD(T) methods with the cc-pVQZ basis set were used for the neutral and ionic species, respectively. Bond lengths are in bohrs and bond angles in degrees

TABLE II
Vertical excitation energies and transition moments between singlet states of S_4

	C_{2v} (I)				D_{2h} (II)			C_{2h} (III)			
State	T_v^a, eV	μ_e^a, D	T_v^b, eV	μ_e^b, D	State	T_v^c, eV	μ_e^c, D	State	T_v^d, eV	μ_e^d, D	T_v^e, eV	μ_e^e, D
X^1A_1	0.000		0.000		X^1A_g	0.000		X^1A_g	0.000		0.000	
A^1A_2	1.722		1.892		A^1B_{2g}	2.142		A^1B_g	1.312		1.235	
B^1B_1	1.935	0.1678 (x)	1.825	0.0760 (x)	B^1B_{1u}	2.220	0.8071 (z)	B^1A_u	1.846	0.2028 (z)	2.381	0.0684 (z)
C^1B_2	2.588	1.8732 (y)	2.244	2.4706 (y)	C^1B_{1g}	2.305		C^1B_u	2.279	2.4881 (x)	1.867	3.3076 (x)
										0.3389 (y)		0.4662 (y)
D^1A_1	3.009	1.1007 (z)	4.055	0.6121 (z)	D^1A_g	2.490		D^1A_g	2.674		4.212	
E^1A_2	3.694		3.615		E^1B_{2g}	2.831		E^1B_g	3.593		3.300	
F^1B_1	3.874	0.1739 (x)	4.026	0.6176 (x)	F^1A_u	2.981		F^1Au	3.873	0.0988 (z)	5.001	0.1538 (z)
G^1B_2	4.716	0.2848 (y)	4.803	0.4263 (y)	G^1B_{3u}	2.994	0.1843 (x)	G^1B_u	4.741	1.7228 (x)	4.557	2.6508 (x)
										1.1518 (y)		0.2783 (y)

[a] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^1A_1: R_1 = 3.677 bohr, R_2 = 4.213 bohr, α = 106.3°; E = −1590.268691 hartree. [b] TD-DFT B3LYP/6-311+G(3df) at the CCSD(T)/cc-pVQZ optimized geometry of X^1A_1. [c] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^1A_1: R_1 = 3.645 bohr, R_2 = 5.164 bohr; E = −1590.266490 hartree. [d] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^1A_g: R_1 = 3.714 bohr, R_2 = 4.109 bohr, α = 108.8°; E = −1590.258913 hartree. [e] TD-DFT B3LYP/6-311+G(3df) at the CCSD(T)/cc-pVQZ optimized geometry of X^1A_g.

eV and for the ^1B_u 2.174 eV, in reasonably good agreement with the SA-CASSCF values. In agreement with Wong and Steudel[30], the *trans*-transition is stronger and lies lower than the *cis*-transition. The experimental information about the neutral S_4 electronic states has been obtained in the gas phase by photodetaching the negative ion. Four bands belonging to S_4 electronic states were observed at 2.42, 2.70, 2.96, and 3.19 eV with monochromatic light source of $h\nu = 4.66$ eV. At least one of the bands must belong to the electronic ground state of one of the isomers, but neither the experiment nor our calculations give excitation energies lying below 1 eV. In Table II the SA-CASSCF method yields low-excited singlet states (two in each irreducible representation) up to about 4.5 eV. The bands might correspond to detachments from several isomers, but the adiabatic and vertical electron affinities calculated by Zakrzewski and von Niessen[21] for more isomers also do not allow any assignment of the observed spectrum.

In Table III optimized geometries, energy differences between the isomers and harmonic wavenumbers for the S_4^+ isomers are given. The *cis*-form is calculated with RCCSD(T)/cc-pVQZ to be degenerate with the rectangular

TABLE III
Optimized geometries and harmonic wavenumbers of the three lowest-lying isomers of S_4^+. Bond lengths are in atomic units and angles in degrees

Method	C_{2v} (I)			D_{2h} (II)		C_{2h} (III)		
	R_1	R_2	α	R_1	R_2	R_1	R_2	α
a	3.525	4.722	95.7	3.521	5.065	3.598	4.030	107.6
b	3.545	4.986	91.9	3.545	5.100	3.622	4.082	107.6
c	3.555	3.944	110.5	3.447	5.087	3575	3.889	107.5
ΔE^a, eV	0.0008			0.0000		0.2765		
	b			b		b		
Modes, cm^{-1} ω_1	757 (a_1)			757 (a_g)		649 (a_g)		
ω_2	246 (a_1)			247 (a_g)		404 (a_g)		
ω_3	33 (a_1)			293 (b_{3g})		193 (a_g)		
ω_4	170 (a_2)			172 (a_u)		69 (a_u)		
ω_5	726 (b_2)			726 (b_{1u})		645 (b_u)		
ω_6	294 (b_2)			38 (b_{2u})		92 (b_u)		

[a] RCCSD(T)/cc-pVQZ.

form (no imaginary wavenumber for the b_{2u} mode inducing automerization is calculated). In Table III the SA-CASSCF vertical excitation energies and the electronic transition moments are presented. In Fig. 2 the RCCSD(T) adiabatic transition energies together with the band strength based on the
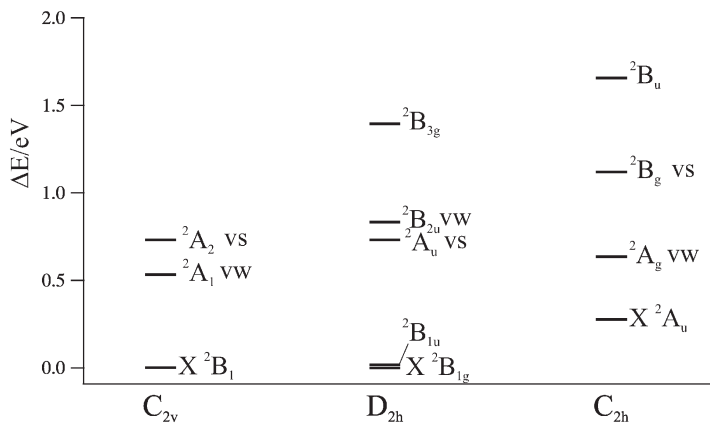

FIG. 2
Adiabatic transition energies (RCCSD(T)/cc-pVQZ) of the lowest doublet states of three S_4^+ isomers. The band strengths are based on transition moments calculated at the SA-CASSCF/cc-pVTZ level of theory
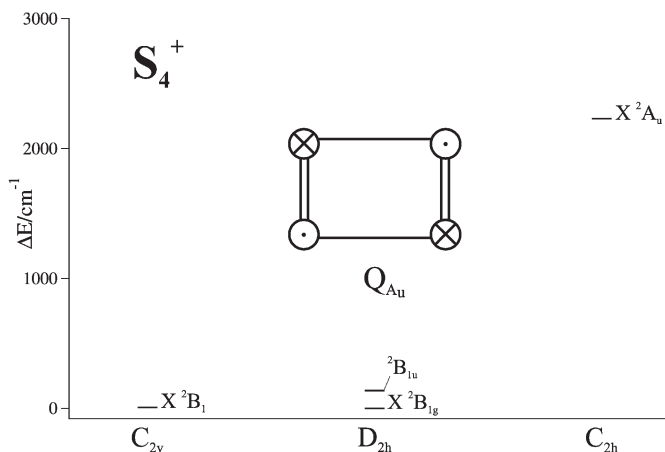

FIG. 3
Optimized ground state energies (RCCSD(T)/cc-pVQZ) of the *cis*-, rectangular and *trans*-isomers of S_4^+. In the rectangular isomer, the $^2B_{1u}$ state, which is almost degenerate with the X^2B_{1g} state, and the relative A_u coupling mode are represented, as well

transition moments of the SA-CASSCF values in Table IV are shown. These results should prove useful for UV spectroscopy after deposition of mass-selected ions in a cold matrix. We found that the $^2B_{1u}$ state has its minimum very close to the rectangular minimum. With the present calculations we cannot definitely say which form is more stable. The rectangular state is vibronically coupled by the a_u mode with the very close-lying $^2B_{1u}$ state (cf. Fig. 3), and the electronic ground state of S_4^+, according to the present rather extensive calculations, posseses a very complex ro-vibronic structure with very flat parts of the 6D potential, making the harmonic approximation used in the calculations of the vibrational wavenumbers not very appropriate. The harmonic pattern in Table III suggests the presence of anharmonic polyads. In Table V the present optimized geometries for low-lying states of S_4^+ are compared with similar data of ref.[21] calculated by the RHF method. Particularly the R_2 distance is very sensitive to the elec-

TABLE IV
Vertical excitation energies and transition moments between doublet states of S_4^+

C_{2v} (I)			D_{2h} (II)			C_{2h} (III)		
State	$T_v{}^a$, eV	μ_e, D	State	$T_v{}^b$, eV	μ_e, D	State	$T_v{}^c$, eV	μ_e, D
X^2B_1	0.000		X^2B_{1g}	0.000		X^2A_u	0.000	
A^2A_1	0.543	0.08575 (x)	A^2A_u	0.710	1.68230 (z)	A^2A_g	0.241	0.07289 (z)
B^2A_2	0.940	1.92834 (y)	B^2B_{2u}	0.713	0.09730 (x)	B^2B_u	0.927	
C^2B_2	1.171		C^2B_{3g}	1.260		C^2B_g	0.981	2.19945 (x)
								0.51297 (y)
D^2B_2	1.533		D^2B_{1u}	1.584		D^2B_u	1.502	
E^2A_1	2.228	0.08352 (x)	E^2B_{3g}	2.025		E^2B_g	1.862	0.15917 (x)
								0.09934 (y)
F^2A_2	2.581	0.11466 (y)	F^2A_g	2.177		F^2A_g	2.314	0.15627 (z)
G^2B_1	3.136	0.33646 (z)	G^2B_{2g}	2.646		G^2A_u	2.740	

[a] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2B_1: R_1 = 3.597 bohr, R_2 = 4.591 bohr, α = 102.4°; E = –1589.990006 hartree. [b] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2B_{1g}: R_1 = 3.576 bohr, R_2 = 5.298 bohr; E = –1589.988830 hartree. [c] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2A_u: R_1 = 3.653 bohr, R_2 = 4.187 bohr, α = 108.3°; E = –1589.981631 hartree.

TABLE V
Optimized geometries and energies of several doublet electronic states of S_4^+. Bond lengths are in atomic units and angles in degrees

State	Method	R_1	R_2	α	ΔE, eV
			C_{2v} (I)[a]		
X^2B_1	[b]	3.525	4.723	95.7	0.000
	[c]	3.555	3.944	110.5	
$^2A_1$	[b]	3.565	4.212	116.2	0.531
	[c]	3.521	4.002	117.5	
$^2A_2$	[b]	3.528	5.519	90.1	0.729
			D_{2h} (II)[b]		
X^2B_{1g}	[b]	3.521	5.065		0.000
	[c]	3.447	5.087		
$^2B_{1u}$	[b]	3.691	4.223		0.017
	[c]	3.632	4.159		
^2A_u	[b]	3.528	5.525		0.730
$^2B_{2u}$	[b]	3.523	5.499		0.833
			C_{2h} (III)[c]		
X^2A_u	[b]	3.598	4.030	107.6	0.000
	[c]	3.575	3.889	107.5	
^2A_g	[b]	3.574	4.269	112.5	0.358
	[c]	3.530	4.021	113.8	
^2B_g	[b]	3.551	4.833	105.6	0.843
^2B_u	[b]	3.546	5.682	106.5	1.380

[a] $\Delta E_{RCCSD(T)}$ relative to the X^2B_1 state of *cis*-S_4^+; $E = -1590.692506$ hartree. [b] $\Delta E_{RCCSD(T)}$ relative to the X^2B_{1g} state of rectangular S_4^+; $E = -1590.692537$ hartree. [c] $\Delta E_{RCCSD(T)}$ relative to the X^2A_u state of *trans*-S_4^+; $E = -1590.682374$ hartree.

tron correlation effects. The differences lie in the range up to 0.24 bohr. A striking difference of about 0.8 bohr for R_2 and 15° for the bond angle is found in the *cis*-form ground state; therefore, the adiabatic energy differences reported previously are not reliable. The published theoretical first vertical ionization energies obtained by the OVGF method for the *cis*- and *trans*-forms of ref.[20] and ref.[21] differ by about 0.3 eV. The appearance potential of S_4^+ was measured to be 10.1 eV [49]. All theoretical calculations found that the first ionization potential lies substantially lower. Our RCCSD(T) adiabatic values amount to 8.80 eV (*cis*), 8.72 eV (D_{2h}), and 8.68 eV (*trans*). In Table VI the optimized geometries of the quartet states and their relative positions to the doublet states are given.

TABLE VI
Optimized geometries and energies of several quartet electronic states of S_4^+. Bond lengths are in atomic units and angles in degrees

State	Method	R_1	R_2	α	ΔE, eV
		C_{2v} (I)^a			
$^4B_2$	b	3.599	5.088	111.9	0.469
$^4A_1$	b	3.781	4.488	93.5	1.157
$^4B_1$	b	3.909	3.973	107.9	2.057
		D_{2h} (II)^b			
$^4B_{3g}$	b	3.577	6.033		0.573
^4A_g	b	3.772	4.723		1.146
^4A_u	b	3.586	7.679		1.169
		C_{2h} (III)^c			
^4B_u	b	3.609	4.981	108.4	0.272
^4B_g	b	3.583	5.875	153.2	0.919
^4A_u	b	3.954	3.929	101.2	1.932

^{a} ΔE_{CASSCF} relative to the X^2B_1 state of *cis*-S_4^+; $E = -1589.992752$ hartree. ^{b} ΔE_{CASSCF} relative to the X^2B_{1g} state of rectangular S_4^+; $E = -1589.992282$ hartree. ^{c} ΔE_{CASSCF} relative to the X^2A_u state of *trans*-S_4^+; $E = -1589.986275$ hartree.

In Tables VII to X similar results are presented for the negative ion. As before, the RHF R_2 optimized distance in the *cis*-form differs by about 0.2 bohr from the RCCSD(T) value (Table IX). The vertical SA-CASSCF and TD-DFT excitation energies (Table VIII) for low-lying states agree to within 0.1 to 0.3 eV. The RCCSD(T) adiabatic electron affinities were calculated to be: 2.24 eV (*cis*), 2.19 eV (D_{2h}) and 2.6 eV (*trans*). The experimental vertical electron detachment energy was reported to be 2.42 eV [22]. Figure 4 shows the adiabatic excitation energies and the band strengths for S_4^- calculated in a similar way as in Fig. 3 for S_4^+.

TABLE VII
Optimized geometries and harmonic wavenumbers of the three lowest-lying isomers of S_4^-. Bond lengths are in atomic units and angles in degrees

Method	C_{2v} (I)			D_{2h} (II)		C_{2h} (III)		
	R_1	R_2	α	R_1	R_2	R_1	R_2	α
[a]	3.724	4.108	107.6	3.685	4.991	3.771	3.946	107.3
[b]	3.749	4.159	107.5	3.711	5.029	3.798	3.991	107.4
[c]	3.689	3.885	114.3	3.642	5.036	3.810	3.821	107.5
ΔE^a, eV	0.0000			0.1259		0.0226		
	[b]			[b]		[b]		
Modes, cm^{-1} ω_1	604 (a$_1$)			650 (a$_g$)		576 (a$_g$)		
ω_2	319 (a$_1$)			250 (a$_g$)		462 (a$_g$)		
ω_3	96 (a$_1$)			281 (b$_{3g}$)		204 (a$_g$)		
ω_4	118 (a$_2$)			176 (a$_u$)		70 (a$_u$)		
ω_5	651 (b$_2$)			613 (b$_{1u2}$)		712 (b$_u$)		
ω_6	282 (b$_2$)			i76 (b$_{2u}$)		128 (b$_u$)		

[a] RCCSD(T)/cc-pVQZ.

TABLE VIII
Vertical excitation energies and transition moments between doublet states of S_4^-

C_{2v} (I)					D_{2h} (II)			C_{2h} (III)				
State	T_v^a, eV	μ_e^a, D	T_v^b, eV	μ_e^b, D	State	T_v^c, eV	μ_e^c, D	State	T_v^d, eV	μ_e^d, D	T_v^e, eV	μ_e^e, D
X^2A_2	0.000		0.000		X^2A_u	0.000		X^2B_g	0.000		0.000	
A^2B_1	1.160	2.84883 (y)	1.401	2.6307 (y)	A^2B_{1g}	0.816	1.67983 (z)	A^2A_u	1.020	3.75549 (x) / 0.20799 (y)	1.167	3.43164 (x) / 0.53225 (y)
B^2A_1	1.412		1.768		B^2B_{3g}	1.313	0.00731 (x)	B^2A_g	1.288		1.434	
C^2B_2	2.125	0.00118 (x)	2.005	0.06710 (x)	C^2B_{2u}	1.516		C^2B_u	2.337	0.06445 (z)	2.298	0.05617 (z)
D^2B_2	2.177	0.14024 (x)	2.271	0.32560 (x)	D^2B_{1u}	1.815		D^2B_u	2.422	0.18824 (z)	2.551	0.28646 (z)
					E^2B_{2u}	1.939						

[a] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2A_2: $R_1 = 3.801$ bohr, $R_2 = 4.198$ bohr, $\alpha = 111.7°$, $E = -1590.305684$ hartree. [b] TD-DFT B3LYP/6-311+G(3df) at the RCCSD(T)/cc-pVQZ optimized geometry of X^2A_2. [c] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2A_u: $R_1 = 3.754$ bohr, $R_2 = 5.278$ bohr; $E = -1590.301386$ hartree. [d] Full-valence state averaged CASSCF and cc-pVTZ basis set at the optimized geometry of X^2B_g: $R_1 = 3.848$ bohr, $R_2 = 4.068$ bohr, $\alpha = 108.3°$; $E = -1590.306402$ hartree. [e] TD-DFT B3LYP/6-311+G(3df) at the RCCSD(T)/cc-pVQZ optimized geometry of X^2B_g.

Optimized geometries and energies of several doublet electronic states of S_4^-. Bond lengths are in atomic units and angles in degrees

State	Method	R_1	R_2	α	ΔE, eV
		C_{2v} (I)[a]			
X^2A_2	b	3.724	4.108	107.6	0.000
	c	3.689	3.885	114.3	
$^2B_1$	b	3.692	5.494	90.2	1.011
$^2B_2$	b	3.922	4.178	95.1	1.127
$^2A_1$	b	3.742	4.683	112.7	1.361
		D_{2h} (II)[b]			
X^2A_u	b	3.685	4.991		0.000
	c	3.642	5.036		
$^2B_{1g}$	b	3.692	5.509		0.885
$^2B_{1u}$	b	3.903	4.497		1.008
$^2B_{3g}$	b	3.690	5.181		1.158
$^2B_{2u}$	b	3.699	5.828		1.404
		C_{2h} (III)[c]			
X^2B_g	b	3.771	3.946	107.3	0.000
	c	3.810	3.821	107.5	
^2A_u	b	3.788	4.198	100.1	0.882
^2A_g	b	3.782	4.420	103.9	1.207
^2B_u	b	4.005	3.883	94.5	1.980

[a] $\Delta E_{RCCSD(T)}$ relative to the X^2A_2 state of *cis*-S_4^-; $E = -1591.098068$ hartree. [b] $\Delta E_{RCCSD(T)}$ relative to the X^2A_u state of rectangular S_4^-; $E = -1591.093441$ hartree. [c] $\Delta E_{RCCSD(T)}$ relative to the X^2B_g state of *trans*-S_4^-; $E = -1591.097239$ hartree.

TABLE X
Optimized geometries and energies of several quartet electronic states of S_4^-. Bond lengths are in atomic units and angles in degrees

State	Method	R_1	R_2	α	ΔE, eV
		C_{2v} (I)[a]			
$^4A_1$	[b]	3.761	6.432	90.1	0.927
$^4B_1$	[b]	3.773	7.648	170.0	1.275
$^4A_2$	[b]	3.778	7.648	170.0	1.424
		D_{2h} (II)[b]			
$^4B_{2u}$	[b]	3.761	6.437		0.764
^4A_u	[b]	3.769	8.000		1.323
		C_{2h} (III)[c]			
^4A_g	[b]	3.789	5.694	113.8	0.959
^4A_u	[b]	3.781	5.671	160.6	1.151
^4B_g	[b]	3.777	8.067	163.7	1.453

[a] ΔECASSCF relative to the X^2A_2 state of cis-S_4^-; $E = -1590.310002$ hartree. [b] ΔE_{CASSCF} relative to the X^2A_u state of rectangular S_4^-; $E = -1590.304028$ hartree. [c] ΔE_{CASSCF} relative to the X^2B_g state of trans-S_4^-; $E = -1590.311577$ hartree.
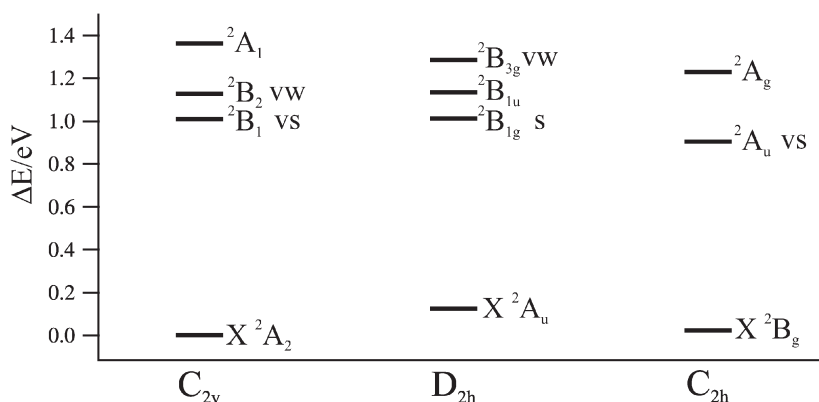

FIG. 4
Adiabatic transition energies (RCCSD(T)/cc-pVQZ) of the lowest doublet states of three S_4^- isomers. The band strengths are based on transition moments calculated at the SA-CASSCF/cc-pVTZ level of theory

CONCLUSIONS

The patterns of electronically excited states in *cis*- and *trans*-isomers of S_4^+ and S_4^- calculated by SA-CASSCF, TD-DFT, and RCCSD(T) methods should allow their detection and the assignments by the UV-absorption matrix spectra using mass-selected beams. In both ions strong anharmonic resonances and close-lying isomers will make studies of nuclear motion dynamics very complex. We have tried to obtain analytic forms of the full six-dimensional potential energy surfaces for the neutral and ionic ground states. Due to the existence of several stable isomers, extremely flat potential parts, and the necessity to use a multiconfigurational approach, calculating the analytic full six-dimensional potential energy surfaces for the ground states remains a demanding task.

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