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Structures, stabilities and adiabatic ionization and electron affinity energies of small sulfur clusters S_3–S_5*

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Summary. The vertical and adiabatic ionization and electron affinity energies are calculated for the isomers of S_3, S_4 and S_5. For the existing isomers the structures of several ionic states were optimized using an RHF analytical gradient approach with a subsequent frequency analysis. The many-body effects were taken into account by Green function (for vertical energies) and CI (for vertical and adiabatic energies) techniques. The structural relaxation upon ionization or attachment of an electron is found to be of primary importance to account for the sequence of cationic states or the existence of a positive electron affinity.

Key words: Small sulfur clusters – S_3–S_5 – Electron affinity energies – Ionization energies

1 Introduction

The structures and stabilities of the clusters of elemental sulfur were intensively studied theoretically during the last few years at different levels of sophistication. The thirteen isomers of S_4 were studied in detail by Quelch et al. [1] who used the analytical gradient geometry optimization at the self-consistent-field (SCF) and configuration interaction (CI) level to determine the stationary points on the potential energy surface and to check their type. The relative stabilities of the isomers were calculated by extensive CI, CASSCF and coupled cluster calculations. The possible isomers of S_2–S_{12} clusters were studied by Raghavachari et al. [2] using SCF, CI and many-body perturbation theory (MBPT) calculations. In order not to repeat the extensive discussion of the results concerning the structures and relative stabilities of different sulfur clusters obtained by different methods we refer to Refs. [1, 2].

The vertical ionization potentials (VIP) and vertical electron affinities (VEA) of S_3 and S_4 were presented in Refs. [3–5]. For the calculation of VIPs and VEAs the

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* Dedicated to Professor W. Kutzelnigg on the occasion of his 60th birthday.

Green function method as well as CI and CASSCF approaches were used. The calculation of the VIP and VEA, however, is not sufficient to provide complete information concerning cationic and anionic states. The detailed examination of the lowest ionic states, their structures and stabilities, supplies valuable information on small sulfur clusters and their isomers. First, as was shown in Refs. [1, 2], even the neutral sulfur clusters may have a large number of structures representing stationary points on the potential energy surfaces and some of them appear to be true minima, whereas others appear to be transition states. We may expect that some structures, being transition states in the neutral S_n cluster, may transform upon ionization or electron attachment into stable cationic or anionic structures and vice versa. Secondly, the existence of many stationary points with small energy differences between them suggests the possibility of a rather shallow character of the potential energy surfaces and therefore one may expect appreciable structural changes accompanying the process of ionization or electron attachment. Third, in the case of electron attachment the structural relaxation may happen to be crucial for the stabilization of the anionic states and in fact responsible for the positive electron affinity. Recently the bound negative ions of S_5–S_{10} were observed [6, 7]. As the VEAS are all positive (at least up to S_8, see the present work and work in progress) there should be some nuclear rearrangements which may be decisive for the chemical reactions. Experimental data are very scarce on S clusters because the individual clusters and their isomers are difficult or impossible to obtain in pure form. We thus aim at replacing this lack of data by reliable theoretical calculations. In the present work we study the adiabatic ionization (AIP) and electron affinity energies (AEA) for the isomers of small sulfur clusters S_3, S_4 and S_5. For S_3 the isomers with C_{2v} (open form), D_{3h} (cyclic) and $D_{\infty h}$ symmetries are considered. For S_4 we study the following isomers: D_{2h} (rectangular ring), D_{4h} (square ring), D_{3h} (branched chain), D_{2d} (puckered ring), C_{2v} (*cis* planar), C_{2h} (*trans* planar), C_{3v} pyramid), C_s (branched ring), and C_2 (helical). For S_5 we study C_s (envelope cyclic), C_2 (twisted cyclic), and C_2 (helical) isomers. The geometry optimization for the ionic states was performed by the analytical gradient technique at the SCF level. The optimized geometries were used to calculate the AIPs and AEAs with large basis sets by the CI method. We also repeated the outer valence Green function (OVGF) [10–13] calculation of VIP with the same basis set.

2 Computational methods

The geometry optimization of the neutral and ionic structures was performed using the analytical gradient technique at the SCF level using the GAMESS program [9]. For the calculation of the open shell ionic (doublet) and the triplet neutral ground states the restricted Hartree–Fock method was employed. For the geometry optimization of the isomers of $S_3, S_3^+, S_3^-, S_4, S_4^+$ and S_4^- the 6–31 + G^* basis set was used and for the optimization of the isomers S_5, S_5^+ and S_5^- the 6–31G* basis set. We used the basis sets included in the GAMESS program. In all cases the harmonic frequency analysis followed the optimization calculations to check whether the stationary point found represents a true minimum or a transition state.

The vertical ionization and electron affinity energies were calculated by the OVGF method [10–13] which takes into account for the self-energy all diagrams up to and including the third-order diagrams with a renormalization procedure for the higher order corrections.

The VIPs, VEAs, AIPs and AEAs were calculated by the CI method. In Ref. [4] it was found that the single-reference CI treatment provides us with reliable results for the VIPs and VEAs of the S_3 and S_4 isomers, although from the structure of the wavefunction a multireference treatment appeared to be advised. For S_3 this is also corroborated by the experimental results. In the true multireference CI there remains the problem of a balanced choice of the reference configurations for the neutral ground and ionic states which appears to be unsolvable at present (see Ref. [4]). Therefore in the present calculations we used the single-reference single-and-double excitation CI. The CI energies were corrected by the Davidson method [14] for the inclusion of the contributions from the quadruple and higher excitations. The MOLCAS-2 suit of programs [15] was used to perform the CI calculations as well as the necessary SCF and integral transformation calculations preceding the OVGF calculation.

In the CI and OVGF calculations the very large atomic natural orbitals (ANO) [16] basis set (17s12p5d4f) was employed. The ANO basis set is especially suited for the calculation of properties where an extensive correlation treatment is necessary and an extended basis set including diffuse functions is required. It involves a minimal contraction loss [17]. For the calculations of ionization and electron affinity energies of the isomers of S_3 and S_4 the ANO basis set was contracted to [6s5p2d1f] and for the S_5 isomers to [6s4p1d]. In all the CI calculations only the core orbitals were kept frozen. In the OVGF calculations again only the core orbitals were omitted except for the calculation on the S_4 isomers with C_s and C_{3v} symmetry. In these latter cases the 13 highest virtual MOs with orbital energies exceeding 3 a.u. were deleted.

Direct estimation of the accuracy represents a difficult problem for the techniques employed in the present study of small sulfur clusters because of the lack of experimental data. Previous calculations on ionization and electron affinity energies of Si_3–Si_{10} [5, 18] show that the methods and basis sets used in the present work provide an agreement with the experimental values within 0.2–0.3 eV. Other basis sets are to our knowledge (see, for example, [3–5]) not as suitable as the ANO basis set for a reliable calculation of the IP and EA data of species containing sulfur datoms.

3 Results and discussion

3.1 S_3 isomers

3.1.1 Structure of the neutral S_3 isomers. The S_3 cluster has three isomers with D_{3h} (the cyclic form), C_{2v} (the open form) and $D_{\infty h}$ (the linear form) symmetries. The structures of these isomers were studied theoretically previously [2, 19–25], however to maintain consistency with the optimization of the ionic state structures we also reoptimized the S_3 neutral isomers with the 6–31 + G* basis set. The geometrical parameters for the neutral S_3 isomers are given in Table 1. The structures of the lowest open and cyclic isomers are given in Fig. 1. The results of the present optimization for the neutral isomers are in agreement with those from Refs. [2, 21] within ~ 0.03 Å in bond lengths and ~ 1° in bond angles.

The total and relative SCF and CI (including the Davidson correction) energies of S_3 isomers are given in Table 2. The open form isomer is lower in energy than the cyclic isomer by only ~ 1.2 kcal/mol according to the results of our CI calculation. In the SCF calculations the cyclic isomer remains more stable and this relative

Table 1. Geometrical parameters (in Å) of S_3, S_3^+ and S_3^- optimized at the HF/6–31 + G* level. The parameter r_{ij} denotes the bond length between atoms i and j. The parameter θ_{ijk} denotes the bond angle formed by bond between atoms ij and jk

Molecule	Symmetry	Electronic state	Parameter	Value
S_3	$D_{\infty h}$	$^1\Sigma_g$	r_{12}	1.984
S_3^+	$D_{\infty h}$	$^2\Sigma_g$	r_{12}	1.820
S_3	D_{3h}	$^1A'_1$	r_{12}	2.065
S_3^-	D_{3h}	$^2A'_2$	r_{12}	2.233
S_3	C_{2v}	$^1A_1$	r_{12}	1.899
			θ_{123}	117.46
S_3^+	C_{2v}	$^2A_2$	r_{12}	1.931
			θ_{123}	110.73
S_3^+	C_{2v}	$^2A_1$	r_{12}	1.854
			θ_{123}	131.36
S_3^+	C_{2v}	$^2B_2$	r_{12}	1.898
			θ_{123}	99.71
S_3^-	C_{2v}	$^2B_1$	r_{12}	1.993
			θ_{123}	114.72
S_3^+	C_s	$^2A'$	r_{12}	1.854
			r_{13}	2.018
			θ_{123}	112.10

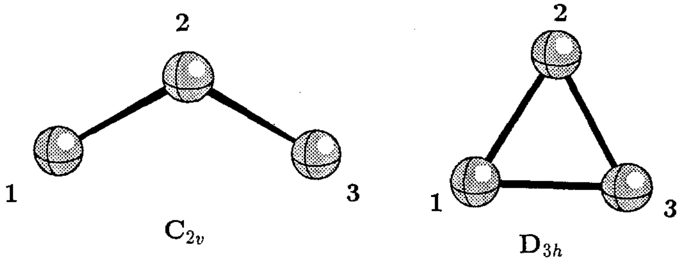


Fig. 1. The open form (C_{2v}) and cyclic (D_{3h}) structures of S_3

stability decreases from 9.3 kcal/mol ((12s7p1d)/[6s4p1d] basis in Ref. [21]), to 7.6 kcal/mol (6–31G*, Ref. [2]) and to 6.3 kcal/mol in the present calculation. On the other hand, the open form isomer becomes more stable than the cyclic one in our CISD calculation by 1.2 kcal/mol only after taking into account the Davidson correction (without this correction the open form is less stable by 2.12 kcal/mol in the present calculation and by 2.3 kcal/mol in Ref. [21]) and this stability increases to 8.5 kcal/mol and 8.2 kcal/mol in QCISD(T) and MCSCF-MRCI calculations from Refs. [2, 21]. Certainly, despite the approximate character of the Davidson correction, these results together demonstrate the importance of higher-order excitations for the problem of the relative stability of S_3 isomers. However, the main goal of the present work is to calculate ionization and electron affinity energies and as we outlined above for this aim multireference CI approach encounters significant difficulties.

Table 2. The total (in a.u.) and relative (in kcal/mol) energies of the S_3 cyclic, open form and linear isomers calculated at the SCF level with the 6–31 + G* basis set and at the CI (with the Davidson correction) level with the ANO basis set

Symmetry	SCF total energy	SCF relative energy	CI total energy	CI relative energy
D_{3h}	– 1192.487020	0.0	– 1193.173973	1.19
C_{2v}	– 1192.474652	7.76	– 1193.175868	0.0
$D_{\infty h}$	– 1192.290034	123.61	– 1193.052313	77.53

Table 3. Vertical and adiabatic ionization energies (in eV) of the S_3 isomers calculated at the Koopmans, OVGF and CI (with the Davidson correction) levels of approximation in the ANO basis set

Molecule	Symmetry	Ionic state	VEA/VIP			AEA/AIP
			Koopmans	OVGF	CI	CI
S_3^-	D_{3h}	$^2A_2'$	– 1.227	0.026	0.029	0.521
S_3^+	D_{3h}	$^2E''$	9.673	9.101	9.088	9.475[a]
S_3^-	C_{2v}	$^2B_1$	1.434	2.005	2.125	2.377
S_3^+	C_{2v}	$^2B_2$	10.465	9.773	9.801	9.527
S_3^+	C_{2v}	$^2A_1$	10.398	9.679	9.800	9.653
S_3^+	C_{2v}	$^2A_2$	9.943	10.050	9.810	9.881
S_3^+	C_s	$^2A'$				9.845[b]
S_3^+	$D_{\infty h}$	$^2\Sigma_g$	8.082	7.456	7.849	7.779

[a] $E_{tot}(^2B_2(C_{2v})) - E_{tot}(^1A'(D_{3h}))$.

[b] The SCF and CI adiabatic ionization energy of S_3 in the C_s symmetry are given relative to the ground state C_{2v} open form structure

We may conclude that these two isomers of S_3 are rather close to each other in energy. The linear isomer is considerably higher in energy than the other two forms (by 77.5 kcal/mol, CI result). Formally for the S_3 molecule there may exist one more structure of C_s symmetry with closed-shell electron configuration. The geometry optimization for this structure, however, converges to the open-form (C_{2v}) isomer.

3.1.2 Vertical ionization and electron affinity energies of S_3 isomers. S_3 in the cyclic form has the valence electronic configuration of $1a_1'^2 1e'^4 2a_1'^2 1a_2''^2 2e'^4 1e''^4 2a_2'^0$. In the open form the electronic ground-state configuration is $1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 1b_1^2 3b_2^2 4a_1^2 1a_2^2 2b_1^0$. From the previous (see Ref. [3]) Green function calculation of the VIPs of S_3 isomers it follows that in the case of the open form isomer the three cationic states $^2A_2$, $^2B_2$ and $^2A_1$ may be very close in energy. In Ref. [3] the following VIPs were obtained: $^2A_2$ (9.78 eV), $^2B_2$ (9.78 eV) and $^2A_1$ (9.91 eV). The present CI and OVGF calculations differ slightly from the results of the previous calculations (see Table 3). The difference between the VIPs into these three cationic states does not exceed ~ 0.1 eV in the CI and ~ 0.37 eV in the OVGF calculation. In Ref. [3] it was found by the Green function calculation using the ADC(3) method [26, 13] that the ionization into the $^2B_2$ and $^2A_1$ states cannot be considered completely as a one-electron process, and satellite lines appear. We also repeated this calculation using the ADC(3) approach and the ANO basis set. This more extended calculation shows that the enlargement of the basis set in this case renders the satellite lines weaker in intensity and as a reasonable approximation we may consider the ionization of the open-form S_3 into the states $^2B_2$ and $^2A_1$ as one-electron processes. Koopmans' theorem gives the wrong sequence of the cationic states in the case of the open form.

For the cyclic isomer we calculated the VIP into the $^2E''$ state and obtained a very good agreement between the CI (9.088 eV) and OVGF (9.101 eV) values which in turn agree with the OVGF (8.89 eV) value from Ref. [3].

The open form isomer has a large VEA into the $^2B_1$ state in the CI (2.125 eV) and the OVGF (2.005 eV) calculations (this anionic state is bound even at the Koopmans' level (1.434 eV)), whereas the lowest $^2A'_2$ anionic state of the cyclic isomer of S_3 is not bound at the Koopman's level (– 1.227 eV) and may be considered as marginally bound in the CI (0.029 eV) and the OVGF (0.026 eV) calculations.

3.1.3 Structures of the cations and anions of S_3 isomers and the adiabatic ionization and electron affinity energies. For the open-form isomer of S_3 we optimized the geometries of the $^2B_2$, $^2A_1$, and $^2A_2$ cationic and the most stable $^2B_1$ anionic states. From the frequency analysis it is found that they are all true minima. Their optimized geometry parameters are given in Table 1.

The open-form isomer undergoes appreciable structural changes due to ionization, especially in the bond angles (see Table 1). The changes of the bond lengths amount to only ~ 0.04 Å, whereas the bond angle of the $^2A_1$ state is larger by ~ 14.°, of the $^2B_2$ state smaller by ~ 17.°, and of the $^2A_2$ state smaller by ~ 6.2° than the bond angle in the neutral ground state. These changes in the geometry lead to very different vibrational progressions for the photoelectron bands, some being extended and others not. This causes that the VIP have an ordering which differs from those of the AIP. In the relaxed structures the lowest ionic state is the $^2B_2$ state with the $^2A_1$ state found at higher energy. The $^2A_2$ state has the largest AIP, however, the energy difference between these three cationic states with relaxed structures is rather small (~ 0.35 eV). The discussion of the AIP of S_3 (D_{3h}) is given below.

As mentioned above the open and cyclic isomers of S_3 may have positive VEAs by attachment of an electron into the LUMO forming the $^2B_1$ and $^2A'_2$ anionic states, respectively. (The other states are lying much higher.) The geometry optimization of these anionic states leads to relaxed structures which are true minima. Their geometrical parameters are given in Table 1. The structural changes of the $^2B_1$ state of the open-form anion are not so pronounced as in the case of ionization: the bond length elongates by ~ 0.094 Å and the bond angle decreases by ~ 2.74°. The structural changes result in an AEA into the $^2B_1$ state of the open form of S_3 of 2.377 eV (CI result) which is ~ 0.25 eV larger than the VEA. The structural changes of S_3^- in the cyclic form ($^2A'_2$ state) are larger: the bond length elongates by ~ 0.17 Å. This change results in a stabilization of the $^2A'_2$ anionic state and the AEA into this state becomes 0.521 eV (see Table 3), whereas the VEA into the same state is only 0.029 eV (CI result).

3.1.4 The cationic state of S_3 with C_s symmetry. In the cyclic form the two highest occupied MOs are of e' and e'' symmetry and hence after ionization from these

MOs the S_3^+ ion should undergo (according to the Jahn–Teller theorem) a distortion leading to a nondegenerate electronic state. After symmetry reduction of D_{3h} to C_{2v} the e' MO splits into a_1 and b_2, and e'' splits into b_1 and a_2. Therefore one may obviously expect that the ionization of the cyclic isomer results in $^2A_2$, $^2B_2$ or $^2A_1$ cationic states of the open-form isomer. However, an attempt to optimize the degenerate $^2E''$ state of the cyclic isomer within the RHF open-shell procedure leads to a total energy lower than the total energies of the $^2A_2$, $^2B_2$ and $^2A_1$ cationic states of the open form (see Fig. 1). Moreover this $^2E''$ state has real frequences (in the SCF approximation). This fact lead us to investigate a structure with a symmetry lower than C_{2v}, namely, the S_3^+ cation with C_s symmetry. It was found that the lowest $^2A'$ cationic state of S_3^+ in C_s symmetry represents a true minimum and at the SCF level of approximation has the lowest total energy among all the possible cations of the S_3 isomers. The AIP to the $^2A'$ state of S_3^+ in C_s symmetry is 8.673 eV at the SCF level with the 6–31 + G* basis set and calculated relative to the neutral ground state. In the CI calculation this AIP is 9.845 eV and is higher than the AIPs into the $^2B_2$ and $^2A_1$ states, but slightly lower than the the AIP into the $^2A_2$ cationic state of the open form of S_3 (see Table 3). The lowest AIP of the D_{3h} isomer is thus 9.475 eV and refers to the process $^1A'_1(D_{3h}) \rightarrow {}^2B_2(C_{2v})$.

3.2 S_4 isomers

The structures, relative stabilities and harmonic frequencies of several neutral S_4 isomers were studied very extensively by Quelch et al. [1] and Raghavachari et al. [2]. In the present work the structures of the isomers with the following symmetries were considered: C_{2v} (planar *cis*-), C_{2h} (planar *trans*-), D_{4h} (planar square ring), D_{2h} (planar rectangular ring), D_{3h} (planar branched ring), D_{2d} (puckered ring), C_{3v} (pyramidal), C_s (branched chain), and C_2 (helical) (see also Fig. 2). For all the structures except for the helical (C_2) we considered the closed-shell singlet ground states. For the helical structure the ^3B triplet state was examined. The electron configurations of the isomers of S_4 under consideration are given in Table 4. In Table 5 the optimized geometrical parameters are given and the enumeration of atoms is given in Fig. 2. Table 6 contains the total and relative energies of the neutral isomers and transition structures of S_4.

3.2.1 Structures of neutral S_4 isomers. The present results of the geometry optimization are generally rather close to the results of Refs. [1, 2]. The C_{2v}, C_{2h}, D_{3h}, C_s, D_{2d}, and C_2 structures represent at the SCF level of approximation represent true minima, whereas the D_{4h}, C_{3v}, and D_{2h} structures appear to be transition states.

The results of the present CI calculations of the relative energies for the isomers of S_4 are again close to those obtained in Ref. [1] in CISD + Q (single-and-double CI with the Davidson correction) with the TZ2P basis set. The *cis*-planar (C_{2v}) isomer remains the lowest one in the present calculation. However there still remains an open question about this conclusion. In Ref. [2] it was found that the geometry optimization of the rectangular ring (D_{2h}) structure at the MP2/6–31G* level gave a true minimum, and the *cis*-planar isomer C_{2v} collapsed into the D_{2h} isomer. The present relative CI energies of the isomers of S_4 differ from the relative energies obtained in Ref. [4] in MRCI calculations with a smaller basis set. Comparing the results of the present calculation with the results from Refs. [1, 2, 4] we may conclude that an enlargement of the basis set at the CISD + Q level reduces the magnitude of the differences in the relative energies, whereas the

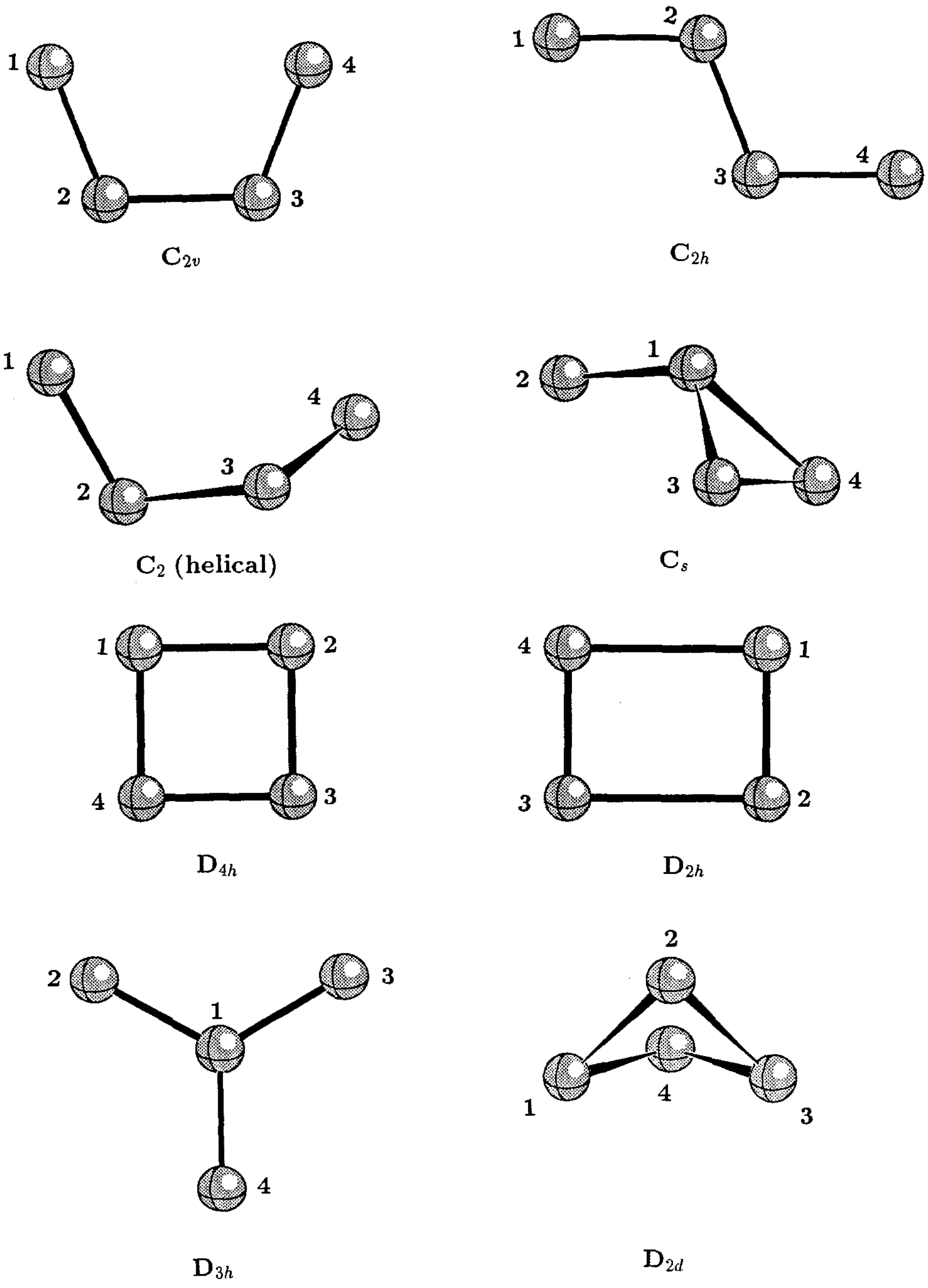


Fig. 2. Structures of S_4 isomers: C_{2v} (planar *cis*-), C_{2h} (planar *trans*-), C_2 (helical), C_s (branched chain), D_{4h} (planar square ring), D_{2h} (planar rectangular ring), D_{3h} (planar branched ring) and D_{2d} (puckered ring)

Table 4. Valence electronic configurations of S_4 isomers

Isomer	Valence electron configuration
$S_4\ C_{2v}$	$1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 4a_1^2 1b_1^2 3b_2^2 1a_2^2 5a_1^2 4b_2^2 2b_1^2 2a_2^{*0}$
$S_4\ C_{2h}$	$1a_g^2 1b_u^2 2a_g^2 2b_u^2 3a_g^2 3b_u^2 1a_u^2 4a_g^2 1b_g^2 4b_u^2 5a_g^2 2a_u^2 2b_g^{*0}$
$S_4\ C_s$	$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 5a'^2 2a''^2 6a'^2 7a'^2 3a''^2 8a''^2 4a''^2 5a''^{*0}$
$S_4\ D_{3h}$	$1a_1'^2 1e'^4 2a_1'^2 2e'^4 1a_2''^2 3e'^4 1e''^4 1a_2'^2 2a_2''^{*0}$
$S_4\ D_{2d}$	$1a_1^2 1e^4 1b_2^2 1b_1^2 2a_1^2 2b_2^2 2e^4 3e^4 3a_1^2 4e^{*0}$
$S_4\ D_{2h}$	$1a_g^2 1b_{3u}^2 1b_{2u}^2 1b_{1g}^2 2a_g^2 3a_g^2 1b_{1u}^2 2b_{3u}^2 1b_{2g}^2 2b_{2u}^2 3b_{3u}^2 1b_{3g}^2 1a_u^{*0}$
$S_4\ D_{4h}$	$1a_{1g}^2 1e_u^4 1b_{2g}^2 1b_{1g}^2 2a_{1g}^2 1a_{2u}^2 2e_u^4 1e_g^4 1b_{1u}^2 3e_u^{*0}$
$S_4\ C_{3v}$	$1a_1^2 1e^4 2a_1^2 3a_1^2 2e^4 3e^4 4a_1^2 4e^4 1a_2^{*0}$

inclusion of higher excitations acts in the opposite direction. Thus, there still remains the question concerning the relative stability of the *cis*- (C_{2v}) and rectangular ring (D_{2h}) isomers. It is to be pointed out that the recent experimental data on the vibronic absorption spectra of S_4 in solid argon [8] are in accord with the conclusion that the *cis*-planar (C_{2v}) isomer represents the ground state of S_4 (see also Fig. 2).

3.2.2 The vertical ionization and electron affinity energies of the isomers of S_4. The results of the present calculations of the VIPs and VEAs performed by OVGF and CI calculations with the ANO basis set are given in Table 7. These results agree with the results from Ref. [4]. The use of the large ANO basis set systematically enlarges the values of the VIPs and VEAs by ~ 0.1–0.3 eV. The results of the CI calculations are in agreement with those of the OVGF calculations again within ~ 0.1–0.3 eV. The vertical ionization and electron attachment processes for the isomers of S_4 were already discussed in detail in Refs. [3, 4].

There is one exception from the general agreement between the OVGF and CI results for the VIP, namely the VIPs of the branched ring (C_s) isomer of S_4. The OVGF calculation predicts the sequence of states $^2A''$ (9.129 eV) and $^2A'$ (9.287 eV), whereas the CI calculation provides the opposite order $^2A'$ (9.001 eV) and $^2A''$ (9.117 eV), although the difference in the VIP in both cases is rather small and these two states are close to each other.

3.2.3 The structures of the low-lying cationic states of the isomers of S_4 and their adiabatic ionization energies. For the isomers of S_4 we studied the optimum geometries of the low-lying cationic states which are formed by ionization of an electron from the HOMO or the next two or three occupied MOs if they are close in energy. The optimized geometrical parameters are collected in Table 5 and structures are given in Fig. 2.

C_{2v}. For the *cis*-planar isomer (C_{2v}) we examined the $^2B_1$, $^2A_1$, and $^2B_2$ cationic states. All these states represent local minima. The structural relaxation upon ionization is quite different among these states. The changes in bond lengths and bond angles for the $^2B_1$ state are rather small (~ 0.03 Å in bond length and ~ 1.0° in bond angle), and larger for the $^2B_2$ state (~ 0.05 Å and ~ 6.0°, respectively) and for the $^2A_1$ state (in bond length ~ 0.04 Å and ~ 4.0° in bond angle) (Table 5). The effect of structural changes is the largest for the $^2B_2$ state. The AIP into this state is ~ 1.1 eV lower than the VIP, so that after the structural relaxation

Table 5. Geometrical parameters (in Å) of S_4, S_4^+ and S_4^- optimized at the HF/6–31 + G* level. The parameter r_{ij} denotes the bond length between atoms *i* and *j*. The parameter θ_{ijk} denotes the bond angle formed by bond between atoms *ij* and *jk*. The parameter ϕ_{ijkl} denotes the dihedral angle between the planes formed by the atoms *ijk* and *jkl*. The notations $r_{ij,kl}$ or $\theta_{ijk,lmn}$ mean $r_{ij} = r_{kl}$ or $\theta_{ijk} = \theta_{lmn}$, respectively

Molecule	Symmetry	Electronic state	Parameter	Value	Type of the point
S_4	C_{2v}	$^1A_1$	$r_{12,34}$	1.916	Minimum
			r_{23}	1.990	
			$\theta_{123,234}$	111.55	
S_4^+	C_{2v}	$^2B_1$	$r_{12,34}$	1.881	Minimum
			r_{23}	2.087	
			$\theta_{123,234}$	110.53	
S_4^+	C_{2v}	$^2A_1$	$r_{12,34}$	1.863	Minimum
			r_{23}	2.118	
			$\theta_{123,234}$	117.54	
S_4^+	C_{2v}	$^2B_2$	$r_{12,34}$	1.953	Minimum
			r_{23}	1.984	
			$\theta_{123,234}$	97.80	
S_4^-	C_{2v}	$^2A_2$	$r_{12,34}$	1.952	Minimum
			r_{23}	2.056	
			$\theta_{123,234}$	114.28	
S_4	C_{2h}	$^1A_1$	$r_{12,34}$	1.933	Minimum
			r_{23}	1.968	
			$\theta_{123,234}$	110.70	
S_4^+	C_{2h}	^2A_u	$r_{12,34}$	1.892	Minimum
			r_{23}	2.058	
			$\theta_{123,234}$	107.50	
S_4^+	C_{2h}	^2A_g	$r_{12,34}$	1.868	Minimum
			r_{23}	2.128	
			$\theta_{123,234}$	113.82	
S_4^-	C_{2h}	^2B_g	$r_{12,34}$	2.016	Minimum
			r_{23}	2.022	
			$\theta_{123,234}$	107.51	
S_4	D_{3h}	$^1A_1$	$r_{12,13,14}$	1.905	Minimum
S_4^+	D_{3h}	$^2A_2'$	$r_{12,13,14}$	1.874	Minimum
S_4^-	D_{3h}	$^2A_2''$	$r_{12,13,14}$	1.990	Saddle
S_4	D_{4h}	$^1A_1$	$r_{12,23,34,14}$	2.114	Saddle
S_4^+	D_{4h}	$^2B_{1u}$	$r_{12,23,34,14}$	2.046	Minimum
S_4	C_{3v}	$^1A_1$	$r_{12,13,14}$	1.990	Saddle
			$\theta_{213,314,214}$	99.998	
S_4^-	C_{3v}	$^2A_2$	$r_{12,13,14}$	2.176	Minimum
			$\theta_{213,314,214}$	110.93	
S_4	D_{2h}	$^1A_1$	$r_{12,34}$	1.870	Saddle
			$r_{13,24}$	2.526	
S_4^+	D_{2h}	$^2B_{3u}$	$r_{12,34}$	1.922	Saddle
			$r_{13,24}$	2.201	

Table 5. (Continued)

Molecule	Symmetry	Electronic state	Parameter	Value	Type of the point
S_4^+	D_{2h}	$^2B_{3g}$	$r_{12,34}$	1.824	Saddle
			$r_{13,24}$	2.692	
S_4^-	D_{2h}	^2A_u	$r_{12,34}$	1.927	Saddle
			$r_{13,24}$	2.665	
S_4	C_s	$^1A'$	r_{12}	1.948	Minimum
			$r_{13,14}$	2.086	
			r_{34}	2.081	
			$\theta_{312,412}$	115.08	
S_4^+	C_s	$^2A'$	r_{12}	2.058	Minimum
			$r_{13,14}$	2.053	
			r_{34}	2.095	
			$\theta_{312,412}$	109.86	
S_4^+	C_s	$^2A''$	r_{12}	2.076	Minimum
			$r_{13,14}$	2.071	
			r_{34}	2.070	
			$\theta_{312,412}$	106.80	
S_4^-	C_s	$^2A''$	r_{12}	2.022	Minimum
			$r_{13,14}$	2.054	
			r_{34}	2.794	
			$\theta_{312,412}$	112.87	
S_4	D_{2d}	$^1A_1$	$r_{12,23,34,41}$	2.106	Minimum
			$\theta_{123,234,341,412}$	85.97	
S_4	C_2	^3B	$r_{12,34}$	1.992	Minimum
			r_{23}	2.089	
			$\theta_{321,432}$	107.48	
			ϕ_{4321}	– 80.98	

Table 6. The total (in a.u.) and relative (in kcal/mol) energies of the S_4 isomers calculated at the SCF level with the 6–31 + G* basis set and at the CI (with the Davidson correction) level with the ANO basis set

Symmetry	SCF total energy	SCF relative energy	CI total energy	CI relative energy
C_{2v}	– 1589.959308	33.38	– 1590.891001	0.0
C_{2h}	– 1589.947638	40.70	– 1590.877730	8.33
D_{3h}	– 1589.935403	48.38	– 1590.862134	18.11
D_{4h}	– 1589.975095	23.48	– 1590.874348	10.45
C_{3v}	– 1589.853625	99.70		
D_{2h}	– 1589.928384	53.56	– 1590.880131	6.82
C_s	– 1589.959289	33.39	– 1590.878790	7.66
D_{2d}	– 1589.982667	18.72	– 1590.885082	3.71
C_2	– 1590.012506	0.0	– 1590.885460	3.48

Table 7. Vertical and adiabatic ionization energies (in eV) of the S_4 isomers calculated at the Koopmans', OVGF, and CI (with the Davidson correction) levels of approximation and with the ANO basis set

Molecule	Symmetry	Ionic state	VEA/VIP			AEA/AIP
			Koopmans	OVGF	CI	CI
S_4^-	C_{2v}	$^2A_2$	1.804	2.082	2.269	2.458
S_4^+	C_{2v}	$^2B_1$	8.581	8.788	8.684	8.555
S_4^+	C_{2v}	$^2A_1$	10.200	9.436	9.556	9.317
S_4^+	C_{2v}	$^2B_2$	10.411	9.746	9.782	8.683
S_4^-	C_{2h}	^2B_g	2.173	2.445	2.686	2.877
S_4^+	C_{2h}	^2A_u	8.496	8.575	8.494	8.344
S_4^+	C_{2h}	^2A_g	9.953	9.174	9.306	9.116
S_4^-	D_{3h}	$^2A_2''$	1.529	2.051	2.291	2.470
S_4^+	D_{3h}	$^2A_2'$	10.111	9.289	9.595[a]	9.511[a]
S_4^-	D_{4h}	^2E_u	− 0.224	1.043	1.076	
S_4^+	D_{4h}	$^2B_{1u}$	8.125	7.641	7.683	7.616
S_4^+	D_{4h}	$^2B_{1u}$	8.125	7.641	7.683	8.046[b]
S_4^-	D_{2h}	^2A_u	1.919	2.118	2.224	2.421
S_4^+	D_{2h}	$^2B_{3g}$	8.209	8.635	8.463	8.398
S_4^+	D_{2h}	$^2B_{3u}$	9.564	9.482	9.377	8.370
S_4^-	C_s	$^2A''$	− 0.469	0.610	0.757	2.046
S_4^+	C_s	$^2A''$	9.513	9.129	9.117	8.939
S_4^+	C_s	$^2A'$	9.634	9.287	9.001	8.905
S_4^-	D_{2d}	^2E	− 0.520	0.714	0.764	
S_4^+	D_{2d}	$^2A_1$	8.735	8.234	8.272	7.908[c]

[a] The CI value without the Davidson correction is used, see the text

[b] This AIP is calculated relative to the ground state of the lowest neutral *cis*- (C_{2v}) isomer.

[c] As the AIP of the $^2A_1$ state of the D_{2d} isomer is given the energy difference between the $^2B_{1u}$ state of the D_{4h} isomer and the ground state energy of the D_{2d} isomer

the sequence of cationic states of the *cis*-planar (C_{2v}) isomer is $^2B_1$ (8.555 eV), $^2B_2$ (8.683 eV) and $^2A_1$ (9.317 eV), whereas the sequence of VIPs is $^2B_1$ (8.684 eV), $^2A_1$ (9.556 eV) and $^2B_2$ (9.782 eV) (CI results, Table 7).

C_{2h}. For the planar *trans*–isomer of S_4 two cationic states ^2A_u and ^2A_g were considered, which appear to be local minima. The geometry changes of the ^2A_u and ^2A_g states do not cause significant lowering of the AIP with respect to the VIP (by ~ 0.15–0.19 eV, Table 7), and the ^2A_u cationic state remains the lowest one.

D_{2h}. For the rectangular ring isomer of S_4 we examined two cationic states: $^2B_{3g}$ and $^2B_{3u}$, which appear to be transition states. The $^2B_{3u}$ state undergoes upon ionization a shortening of the long bond length from 2.526 Å to 2.201 Å with a minor change of the short bond length. The changes of the bond lengths in the $^2B_{3g}$ state are not so pronounced. These structural changes yield such a significant lowering of the $^2B_{3u}$ state (AIP 8.370 eV), that it marginally falls below the $^2B_{3g}$ state (AIP 8.398 eV). The calculation of the VIPs in this case leads to the $^2B_{3g}$ state lying below the $^2B_{3u}$ state. In fact the difference between the AIPs is very small

(~ 0.028 eV) and both states may be considered as nearly degenerate. Due to the fact that the lowest cationic states of the rectangular isomer in our calculation appear to be transition states we may expect that these states are the transition states into the cationic states ${}^2B_1$ and ${}^2B_2$ of the *cis*- (C_{2v}) isomer.

C_s. For the branched ring isomer of S_4 the ${}^2A''$ and ${}^2A'$ cationic states were examined and both states represent local minima. The structural relaxation upon ionization is of minor importance here, yet the changes reduce the already small energy difference between these two states and they become nearly degenerate. In the CI calculation the ${}^2A'$ state is ~ 0.04 eV lower than the ${}^2A''$ state.

D_{3h}. In the branched-chain isomer (D_{3h}) of S_4 the ionization from the HOMO leads to the ${}^2A'_2$ cationic state. The next two MOs are of e'' and e' symmetry and therefore ionization from these MOs leads to a Jahn–Teller distortion. The optimized ${}^2A'_2$ cationic state appears to be a local minimum with the bond length shorter by ~ 0.3 Å than in the ground state. The AIP is ~ 0.08 eV lower than the VIP. In this case we used the CI total energies without the Davidson correction because this correction for the total energy of the cation at the geometry of the ground state is appreciably larger than the correction to the total energy of the cation at the optimized geometry. The different magnitude of the Davidson correction has a consequence that with the Davidson correction the VIP would be smaller than the AIP – an unacceptable result. The different magnitude of the Davidson correction may arise from an avoided crossing in the former case.

D_{4h}, D_{2d}. The upper MOs of the square ring (D_{4h}) isomer are of b_{1u} (HOMO), e_g and e_u symmetry. Therefore, only the ionization from HOMO may lead to a stable cationic state of D_{4h} symmetry. The optimized ${}^2B_{1u}$ cationic state appears to be a local minimum, whereas the neutral square ring isomer represents a transition state. Moreover, the puckered ring isomer (D_{2d}) has a similar electronic structure: the HOMO is of a_1 symmetry whereas the next lower MOs are of e symmetry. Thus the ionization from the HOMO may lead to a cation of D_{2d} symmetry. However, in the geometry optimization of the ${}^2A_1$ cationic state of the puckered ring isomer this state collapsed into the ${}^2B_{1u}$ state of the square ring. The AIP into the ${}^2B_{1u}$ state of the square ring (D_{4h}) isomer is 7.616 eV, i.e. ~ 0.94 eV lower than the AIP into the ${}^2B_1$ state of the *cis*- (C_{2v}) isomer. Therefore, the ${}^2B_{1u}$ state of the square ring isomer becomes the lowest cationic state among the cations of S_4.

C_2. The helical (C_2) isomer of S_4 has a triplet ground state. The optimization procedure for the ${}^2B$ cationic state of this isomer converges to the ${}^2B_2$ cationic state of the *cis*- (C_{2v}) isomer. The attempts to optimize the ${}^2A$ state within the restricted HF SCF procedure did not yield the correct electronic state.

3.2.4 The structure of anionic states and the AEA of the S_4 isomers. For the isomers of S_4 the anionic states obtained by the attachment of an electron into the LUMO were studied. We did not study the anionic states which are formed by the attachment of an electron to the doubly-degenerate LUMOs. (This is the case for the D_{4h} and the D_{2d} isomers.) This point will be discussed below. Neither did we study the shake-up EA states discussed in Ref. [4]. These states can only be discussed in a CI approach.

The results of the geometry optimization and subsequent frequency analysis provide the following anionic states which appear to be local minima: for the *cis*-isomer (C_{2v}) ${}^2A_2$; for the *trans*-isomer (C_{2h}) ${}^2B_g$; for the branched ring (C_s) ${}^2A''$. For the *cis*- and *trans*-isomers the changes in the structural parameters upon the attachment of an electron are not very large (see Table 5): the bonds are elongated by ~ 0.04 ÷ 0.06 Å and the changes in bond angles do not exceed ~ 3.0°. These structural changes therefore do not cause significant changes in the AEA as compared to the VEA. The AEAs for the *cis*- and *trans*-isomers are increased compared to the VEAs by ~ 0.2 eV and they are: for the *cis*-isomer 2.458 eV and for the *trans*-isomer 2.877 eV.

For the branched ring (C_s) isomer the structural changes are more important. The changes in three of the bond lengths are not large, but the fourth bond length (denoted in Table 5 and Fig. 2 as r_{34}) increases by ~ 0.7 Å. In fact the attachment of an electron leads to the breaking of this bond. In turn the AEA is becoming much larger (2.046 eV) than the VEA (0.757 eV). Ionization does not lead to the breaking of this bond.

For the branched chain (D_{3h}) and rectangular ring (D_{2h}) the anionic states ${}^2A_2''$ and ${}^2A_u$, respectively, appear to be transition states. The attachment process of an electron is accompanied by comparatively small changes of structure, and the AEAs into these states are larger by ~ 0.2 eV than the VEAs. We may assume that the anionic state ${}^2A_u$ of the rectangular ring structure is the transition state into the ${}^2A_2$ anionic state of the *cis*- (C_{2v}) isomer, and the ${}^2A_2''$ anionic state of the branched chain isomer (D_{3h}) is the transition state into the ${}^2A''$ anionic state of the branched ring (C_s) isomer.

For the square ring (D_{4h}) and puckered ring (D_{2d}) isomers the LUMO belongs to the doubly degenerate representations of the molecular symmetry groups and therefore the attachment of an electron leads to states which should undergo distortions leading to structures with lower symmetries. We considered the distortion of the puckered ring isomer to C_{2v} symmetry. The reduction of D_{2d} to C_{2v} splits MOs of e symmetry into b_1 and b_2. The SCF calculation on the ${}^2B_1$ state of the D_{2d} form distorted to C_{2v} symmetry does not produce a correct electronic state (the LUMO has an orbital energy lower than the singly occupied MO). Optimization of the ${}^2B_2$ anionic state collapsed to the ${}^2B_{2u}$ anionic state of the rhombus (D_{2h}) structure and this state appears to have two imaginary frequencies.

The electronic structure of the neutral square ring isomer after reduction of D_{4h} to C_{2v} is: $1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 4a_1^2 1b_1^2 3b_2^2 5a_1^2 1a_2^2 2b_1^2 2a_2^2 4b_2^{*0} 6a_1^{*0}$. This occupation differs from the single-reference occupation of the *cis*- (C_{2v}) isomer (see Table 4). The same holds also for the reduction of D_{4h} to D_{2h} and to C_{2h}. Therefore, the straightforward distortion of the ring isomer results in unbound anionic states of the isomers of lower symmetry. On the other hand, the *cis*-isomer in fact should be described by the two-configurational wave function (TSCF) with two electrons in the $2b_1$ and $2a_2$ MOs yielding the ${}^1A_1$ electronic state (see Ref. [1]). Hence, the Jahn–Teller distortion of the ${}^2E_u$ anionic state of the square ring isomer to the lower symmetry more probably involves electronic states which can only be described by multiconfigurational wavefunctions.

The examination of the ${}^2B$ anionic state of the helical (C_2) isomer has shown that this state collapses into the ${}^2B_g$ anionic state of the *trans*-C_{2h} isomer.

The pyramidal (C_{3v}) structure of S_4, being itself a transition state should upon electron attachment give the ${}^2A_2$ anionic state which is a local minimum. However, as the SCF procedure in the ANO basis set was not convergent we are not able to present the CI results for this anion. According to previous calculations (see Refs. [4, 5]) the pyramidal structure of S_4 has a rather large VEA (~ 3.3 eV). Because, the neutral pyramidal structure of S_4 is a high energy isomer this anionic state may hardly exist and further calculations were deemed unnecessary.

3.3 S_5 isomers

The structures, relative stabilities and harmonic frequencies of neutral S_5 isomers were studied by Raghavachari et al. [2]. In this work we consider the structures of the isomers and their cations and anions with the following symmetries: C_s ("half-chair" ring), C_2 (cyclic) and C_2 (helical, with a triplet ground state). In Table 8 the optimized geometrical parameters are given, Table 9 contains the total and relative energies of the neutral isomers and the calculated VIP, AIP, VEA, and AEA values are listed in Table 10. In Table 8 the atoms are numbered according to Fig. 3.

3.3.1 Structures of neutral S_5 isomers. The present results of the geometry optimization and the relative stabilities are rather close to the results of Ref. [2]. The C_s isomer represents the ground state isomer, whereas the C_2 cyclic structure represents a transition state (with one very small imaginary frequency $\sim 33.9\ \mathrm{cm}^{-1}$) and lies above the C_s isomer by only 0.12 kcal/mol (CI result). The helical C_2 isomer with a triplet ground electronic state lies ~ 17.0 kcal/mol above the ground state C_s isomer.

3.3.2 Cationic structures and ionization energies of S_5 isomers. The ground state S_5 (C_s) isomer has the HOMO a'' and the next occupied MO a'. The ionization from these two MO's leads to the cationic states $^2A''$ and $^2A'$ with VIP of 8.220 eV and 9.176 eV (CI result) which are in good agreement with the OVGF results (see Table 10). The optimization of the corresponding cationic states provides structures which are according to the frequency analysis saddle points. The $^2A''$ and $^2A'$ states of S_5 (C_s) maintain the closed ring structure. However, the $^2A''$ cationic state of S_5 has in the SCF calculation with the 6–31 G* basis set a rather small imaginary frequency $\sim 70.0\ \mathrm{cm}^{-1}$. Therefore, we optimized a cationic structure with C_1 symmetry starting from the ring structure of C_s symmetry. The lowering of the symmetry from C_s to C_1 leads to a true minimum at the ^2A cationic state. This cationic state also maintains the closed ring structure. The SCF energy of this state is ~ 0.006 eV lower than the SCF energy of the $^2A''$ cationic state of the C_s isomer. However, the CI calculation reveals the $^2A''$ to be ~ 0.024 eV lower than the ^2A cationic state of the C_1 ring structure. Hence, we may conclude that electron correlation stabilizes the structure which in the SCF calculation has a small imaginary frequency. Probably the optimization of the $^2A''$ cationic state of S_5 (C_s) in a CI, MBPT or MCSCF calculation would provide the true minimum. We may also conclude that the potential energy surface of S_5^+ is rather shallow and thus minima are difficult to find. The geometry changes from C_s to C_1 are significant, although the total energies are nearly the same.

Starting from different initial geometries it is possible to optimize the geometry of another $^2A'$ cationic state of S_5 with C_s symmetry which turns out to have a chain structure representing a local minimum. This $^2A'$ cationic state has the same electronic configuration as the $^2A'$ saddle point but a different order of occupied MOs and is ~ 1.07 eV and ~ 0.34 eV, respectively, higher than the two cationic states of S_5 (C_s) discussed above. Ionization into this $^2A'$ cationic state breaks the bond denoted in Table 8 as r_{45} and thus opens the ring.

The cyclic S_5 (C_2) isomer has a stable ^2B cationic state which has an AIP which is higher in energy than the $^2A''$ cationic state by ~ 0.3 eV (see Table 10).

For the S_5 (C_2) helical isomer ^2A and ^2B cationic states were examined and the first appears to be a local minimum, whereas the second is a transition state, however, with a rather small imaginary frequency ($\sim 57.0\ \mathrm{cm}^{-1}$). Inclusion of

Table 8. Geometrical parameters (in Å) of S_5, S_5^+ and S_5^- optimized at the HF/6–31G* level. The parameter r_{ij} denotes the bond length between atoms i and j. The parameter θ_{ijk} denotes the bond angle formed by bond between atoms ij and jk. The parameter ϕ_{ijkl} denotes the dihedral angle between the planes formed by the atoms ijk and jkl. The notations $r_{ij,kl}$ or $\theta_{ijk,lmn}$ mean $r_{ij} = r_{kl}$ or $\theta_{ijk} = \theta_{lmn}$, respectively

Molecule	Symmetry	Electronic state	Parameter	Value	Type of the point
S_5	C_s	$^1A'$	$r_{12,13}$	2.062	Minimum
			$r_{24,35}$	2.071	
			r_{45}	2.133	
			θ_{213}	94.55	
			$\theta_{124,135}$	99.12	
			ϕ_{4213}	60.20	
			ϕ_{5312}	– 60.20	
S_5^+	C_s	$^2A''$	$r_{12,13}$	2.051	Saddle
			$r_{24,35}$	2.091	
			r_{45}	1.988	
			θ_{213}	96.16	
			$\theta_{124,135}$	97.75	
			ϕ_{4213}	57.57	
			ϕ_{5312}	– 57.57	
S_5^+	C_s	$^2A'$	$r_{12,13}$	2.014	Saddle
			$r_{24,35}$	2.069	
			r_{45}	2.139	
			θ_{213}	103.18	
			$\theta_{124,135}$	104.09	
			ϕ_{4213}	43.55	
			ϕ_{5312}	– 43.55	
S_5^+	C_s	$^2A'$	$r_{12,13}$	2.095	Minimum
			$r_{24,35}$	1.906	
			r_{45}	3.043	
			θ_{213}	93.92	
			$\theta_{124,135}$	106.52	
			ϕ_{4213}	70.98	
			ϕ_{5312}	– 70.98	
S_5^-	C_s	$^2A'$	$r_{12,13}$	1.996	Saddle
			$r_{24,35}$	3.123	
			r_{45}	1.898	
			θ_{213}	111.76	
			$\theta_{124,134}$	90.34	
			ϕ_{4213}	65.79	
			ϕ_{5312}	– 65.79	
S_5^-	C_s	$^2A''$	$r_{12,13}$	2.071	Minimum
			$r_{24,35}$	2.049	
			r_{45}	3.018	
			θ_{213}	100.52	
			$\theta_{124,135}$	104.42	
			ϕ_{4213}	67.97	
			ϕ_{5312}	– 67.97	

Table 8. (Continued)

Molecule	Symmetry	Electronic state	Parameter	Value	Type of the point
S_5	C_2 (cyclic)	^1A	$r_{12,13}$	2.109	Saddle
			$r_{24,35}$	2.057	
			r_{45}	2.066	
			θ_{213}	102.61	
			$\theta_{124,135}$	101.67	
			ϕ_{4213}	19.52	
			ϕ_{5312}	19.52	
S_5^+	C_2 (cyclic)	^2B	$r_{12,13}$	2.037	Minimum
			$r_{24,35}$	2.081	
			r_{45}	2.041	
			θ_{213}	106.10	
			$\theta_{124,135}$	101.06	
			ϕ_{4213}	18.67	
			ϕ_{5312}	18.67	
S_5^-	C_2 (cyclic)	^2B	$r_{12,13}$	2.409	Saddle
			$r_{24,35}$	2.047	
			r_{45}	2.091	
			θ_{213}	89.66	
			$\theta_{124,135}$	108.42	
			ϕ_{4213}	18.38	
			ϕ_{5312}	18.38	
S_5	C_2 (helical)	^3B	$r_{12,45}$	1.994	Minimum
			$r_{23,34}$	2.073	
			θ_{432}	105.62	
			$\theta_{321,543}$	107.95	
			ϕ_{4321}	84.47	
			ϕ_{5432}	84.47	
S_5^+	C_2 (helical)	^2A	$r_{12,45}$	1.893	Minimum
			$r_{23,34}$	2.075	
			θ_{432}	92.16	
			$\theta_{321,543}$	110.19	
			ϕ_{4321}	120.57	
			ϕ_{5432}	120.57	
S_5^+	C_2 (helical)	^2B	$r_{12,45}$	1.899	Saddle
			$r_{23,34}$	2.098	
			θ_{432}	101.70	
			$\theta_{321,543}$	107.92	
			ϕ_{4321}	65.02	
			ϕ_{5432}	65.02	
S_5^-	C_2 (helical)	^2A	$r_{12,45}$	2.006	Minimum
			$r_{23,34}$	2.071	
			θ_{432}	105.94	
			$\theta_{321,543}$	108.08	
			ϕ_{4321}	71.21	
			ϕ_{5432}	71.21	

Table 8. (Continued)

Molecule	Symmetry	Electronic state	Parameter	Value	Type of the point
S_5^-	C_2 (helical)	^2B	$r_{12,45}$	1.998	Minimum
			$r_{23,34}$	2.072	
			θ_{432}	99.43	
			$\theta_{321,543}$	109.99	
			ϕ_{4321}	107.42	
			ϕ_{5432}	107.42	
S_5^+	C_1 (ring)	^2A	r_{12}	2.0370	Minimum
			r_{13}	2.0368	
			r_{24}	2.0807	
			r_{35}	2.0807	
			r_{45}	2.0416	
			θ_{213}	106.079	
			θ_{421}	101.073	
			θ_{135}	101.069	
			θ_{354}	96.3249	
			θ_{245}	96.315	
			ϕ_{2453}	60.56	
			ϕ_{1354}	− 49.41	
			ϕ_{1245}	− 49.41	
			ϕ_{2135}	18.68	
			ϕ_{3124}	18.68	
S_5^-	C_1 (helical)	^2A	r_{12}	2.061	Minimum
			r_{23}	2.071	
			r_{34}	2.085	
			r_{45}	1.987	
			θ_{321}	110.00	
			θ_{432}	108.09	
			θ_{543}	109.03	
			ϕ_{4321}	− 80.31	
			ϕ_{5432}	− 82.17	

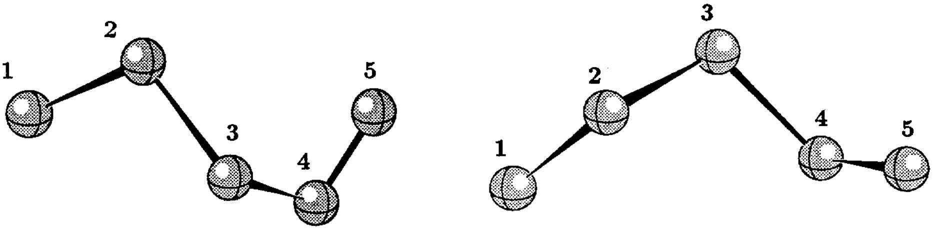
Table 9. The total (in a.u.) and relative (in kcal/mol) energies of the S_5 (C_s), (C_2 *cyclic*) and (C_2 *helical*) isomers calculated at the SCF level with the 6–31G* basis set and at the CI (with the Davidson correction) level with the ANO basis set

Symmetry	Electronic state	SCF total energy	SCF relative energy	CI total energy	CI relative energy
C_s	$^1A'$	− 1987.517748	0.72	− 1988.449535	0.0
C_2 cyclic	^1A	− 1987.517659	0.78	− 1988.449343	0.12
C_2 helical	^3B	− 1987.518901	0.0	− 1988.422214	17.02

electron correlation might convert the ^2B cationic state into a minimum (see the discussion above). The AIP into the ^2A and ^2B cationic states of the helical S_5 isomer are 8.653 eV and 9.083 eV, respectively. However, the ground state of the helical S_5 (C_2) isomer itself lies above the ground state of the S_5 (C_s) isomer by

C_2 (cyclic)

C_s



C_2 (helical)

C_1 (helical)

Fig. 3. Structures of S_5 isomers: C_2 (cyclic), C_s (envelope), C_2 (helical) and C_1 (helical) of S_5^-

Table 10. Vertical and adiabatic ionization energies (in eV) of the S_5 isomers calculated at the Koopmans', OVGF, and CI (with the Davidson correction) levels of approximation and with the ANO basis set

Molecule	Symmetry	Ionic state	VEA/VIP			AEA/AIP
			Koopmans	OVGF	CI	CI
S_5^+	C_s	$^2A''$	9.104	8.215	8.220	8.201
S_5^+	C_1	^2A				8.225[a]
S_5^+	C_s	$^2A'$ (1)	9.858	9.050	9.176	8.933
S_5^+	C_s	$^2A'$ (2)				9.274
S_5^-	C_s	$^2A'$	− 1.257	− 0.083	− 0.099	0.859
S_5^-	C_s	$^2A''$	− 1.271	− 0.105	− 0.110	1.582
S_5^+	C_2 (cyclic)	^2B	9.000	8.189	8.271	8.221
S_5^-	C_2 (cyclic)	^2A	− 1.237	− 0.057	− 0.074	0.818
S_5^-	C_2 (cyclic)	^2B	− 1.283	− 0.126	− 0.145	0.661
S_5^+	C_2 (helical)	^2A			9.177	8.653
S_5^+	C_2 (helical)	^2B			9.319	9.083
S_5^-	C_2 (helical)	^2A			2.021	2.063
S_5^-	C_2 (helical)	^2B			2.095	2.228
S_5^-	C_1 (helical)	^2A				1.533[b]

[a] As the AIP of the S_5 (C_1) isomer the energy difference between S_5^+ (C_1) ^2A state and the ground state of S_5 (C_s) is given.

[b] As the AEA of the S_5 (C_1) isomer the energy difference between S_5^- (C_1) ^2A state and the ground state of S_5 (C_s) is given

~ 0.74 eV and the cationic states of the helical structure are above the cationic states of the S_5 (C_s) isomer.

3.3.3 Anionic structures and electron affinity energies of S_5 isomers. OVGF and CI calculations of the VEA for the most stable S_5 (C_s) isomer do not provide stable anionic states: the VEA remains negative at the Koopmans', OVGF and CI levels of approximation (see Table 10). The helical (C_2) isomer has on the other hand, a positive VEA into the ^2A (2.021 eV) and the ^2B (2.095 eV) state (CI results). Therefore, one may expect the existence also of stable anionic states for the first two isomers. The structural relaxation upon attachment of an electron leads to a stabilization of these anionic states and the AEA's into these states are 2.063 eV and 2.228 eV, respectively. The states are local minima.

We performed the geometry optimization for the two anionic states $^2A''$ and $^2A'$ of S_5 (C_s) formed by attachment of an electron into the LUMO and the next virtual MO. The $^2A''$ cationic state of S_5 (C_s) represents a local minimum. From the data in Table 8 it follows that attachment of an electron breaks the bond between the atoms 4 and 5 (see Fig. 3). Other changes in the structural parameters are not so pronounced. The opening of the ring stabilizes the $^2A''$ anionic state of S_5 (C_s) and the AEA into this state is 1.582 eV (CI result).

The $^2A'$ anionic state of S_5 (C_s) represents a transition state. The AEA into this state is also positive (0.859 eV). However, examination of the structural parameters (see Table 8) leads to the conclusion that this state is a transition state for the decay of the $^2A'$ anionic state of S_5 (C_s) into S_3^- (C_{2v}) + S_2. The Mulliken population analysis data from the SCF calculation shows that the negative charge is distributed between the atoms denoted in Table 8 and Fig. 3 as 1, 2, and 3. The bond distances r_{12} and r_{13}, and the bond angle θ_{213} are close to those of the $^2B_1$ anionic state of S_3 (C_{2v}). The bond distance r_{45} is close to the bond distance in S_2 (see, for example Ref. [2]).

Geometry optimization for the ^2A and ^2B states of the cyclic S_5 (C_2) isomer does not provide states which represent local minima but lead to transition states. The AEAs into these states are 0.818 eV and 0.661 eV, respectively. Probably these states are the transition states into the $^2A'$ and $^2A''$ anionic states of the S_5 (C_s) isomer.

We also tried to obtain an anionic state starting from the S_5 planar *cis–trans*-(C_s) isomer, which was found in Ref. [2] to be a local minimum also. However, the presence of an extra electron causes distortions to a nonplanar structure and finally we obtained another anion of S_5 with C_1 symmetry representing also a local minimum. The AEA into the ^2A anionic state of this S_5 (C_1) isomer calculated relative to the ground state of the S_5 (C_s) isomer is 1.533 eV.

3.3.4 Some energies of the reactions between cations and anions of S_3, S_4 and S_5. In order to estimate the reaction energies of the type $S_4 + S_4^+ \rightarrow S_5 + S_3^+$ etc. we performed the calculation of the CI total energies of the lowest neutral, cationic and anionic states of S_3 and S_4 using the ANO basis set contracted in the same way as for the calculations on S_5. The results of this study are as follows. The reaction of S_4 (C_{2v}) + S_4^+ (D_{4h}, $^2B_{1u}$) results in S_3(C_{2v}) + S_5^+ (C_s, $^2A''$) with an energy release of 18.00 kcal/mol. The reaction of S_4 (C_{2v}) + S_4^+ (D_{4h}, $^2B_{1u}$) results in S_3^+ (C_{2v}, $^2B_2$) + S_5 (C_s) with an energy release of − 8.12 kcal/mol. Therefore the charge exchange reaction $S_3^+ + S_5 \rightarrow S_3 + S_5^+$ should take place. This result is in accord with the conclusion of Ref. [7] that among the S_n^+ ions the most stable is S_5^+.

The reaction of S_4 (C_{2v}) + S_4^- (C_{2v}, $^2A_2$) results in S_3^- (C_{2v}, $^2B_1$) + S_5 (C_s) with an energy release of 18.64 kcal/mol and the reaction of S_4 (C_{2v}) + S_4^- (C_{2v}, $^2A_2$) results in S_3 (C_{2v}) + S_5^- (C_s, $^2A''$) with an energy release of 3.18 kcal/mol. Therefore, the charge exchange reaction $S_5^- + S_3 \rightarrow S_5 + S_3^-$ should occur. In the latter treatment the zero-point vibrations energies are not taken into account because the frequencies are calculated at the SCF level and with different basis sets. However, their inclusion should not effect strongly the conclusions.

The consideration of the reactions is at the present time preliminary because other reactions involving $S_2, S_6, S_7, \ldots$ and their ions should also be taken into account.

4 Conclusions

We have studied many ionic structures of the isomers of S_3, S_4 and S_5 and calculated the AIPs and AEAs using the CI method and the very large ANO basis set. It was found that the ionization and electron attachment processes may result in significant structural relaxation leading to the sequence of states different from that of the vertical states. This, for example, occurs for S_3 (C_{2v}) and S_4 (C_{2v}) cationic states. The $^2B_2$ cationic state of S_3 (C_{2v}) is the lowest one only due to the structural relaxation. For the S_4 (C_{2v}) isomer the structural relaxation changes the sequence of cationic states from $^2B_1, {}^2A_1, {}^2B_1$ (VIPs) to $^2B_1, B_2, {}^2A_1$ (AIPs).

The neutral S_4 (D_{3h}) and S_5 (C_2, helical) isomers are minima, whereas the $^2A_2''$ anionic state of S_4 (D_{3h}) and the ^2B cationic state of S_5 (C_2, helical) are saddle points. The $^2B_{1u}$ cationic state of S_4 (D_{4h}) and the ^2B cationic state of S_5 (C_2, cyclic) are minima, whereas S_4 (D_{4h}) and S_5 (C_2, cyclic) represent saddle points. Thus, the ionization or attachment of an electron may convert the stable neutral isomers into transition states and vice versa.

The lowest cationic states are $^2B_2$ for S_3 (C_{2v}), $^2B_{1u}$ for S_4 (D_{4h}) and $^2A''$ for S_5 (C_s). The lowest AIPs decreases from S_3 (9.527 eV) to S_4 (8.046 eV for the process S_4 (C_{2v}) $\rightarrow S_4^+$ ($^2B_{1u}$, D_{4h}) and slightly increases to S_5 (8.201 eV). The lowest anionic states are $^2B_1$ for S_3 (C_{2v}), $^2A_2$ for S_4 (C_{2v}) and $^2A''$ for S_5 (C_s). The AEA increases from S_3 (2.377 eV) to S_4 (2.458 eV) and decreases from S_4 to S_5 (1.582 eV). The reason is probably that the S_3 and S_4 isomers are chainlike with a good opportunity for the additional electron to become attached to the ends, whereas S_5 is a ring.

The structural relaxation is of primary importance for the process of an electron attachment to S_5 isomers. Thus, the ground-state S_5 (C_s) isomer has a negative VEA but a rather appreciable AEA. The attachment of an electron to S_5 (C_s) leads to the breaking of a bond and the opening of the ring. The present results on the cationic structures of S_3, S_4 and S_5 are in accord with the experimental conclusion that the cations of S_5 are the most stable among the cations of S_n.

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