

The quantum chemical study of the electronic states of S₂Cl and its monovalent ions

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Abstract High-level quantum chemical techniques have been utilized to accurately describe the geometrical parameters, vibrational frequencies and dissociation pathways of the X ²A", 1 ²A', 2 ²A', 2 ²A" states of S₂Cl; X ¹A', 1 ³A", 1 ¹A", 1 ³A' states of S₂Cl⁺; X ¹A', 1 ³A', ¹A" states of S₂Cl⁻, and the corresponding excitation energies have been obtained from the energies extrapolated to their complete basis set limits. It has been established that the 2 ²A' and 2 ²A" terms of S₂Cl exhibit a strong multi-reference character, while all the remaining excited states are dominated by the single replacements from the reference determinants. The enthalpies of the decomposition reactions have been obtained to aid in the investigations into the photolysis of S₂Cl₂ and related systems. The value of the ionization potential of S₂Cl has been found within the error bars of the experiment, and a reliable estimate of its electron affinity, EA₀ = -2.352 eV, has been proposed.

Keywords CBS · CCSD(T) · Excitations · MRCI · S₂Cl

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Introduction

Chlorodisulfane, S₂Cl, is the primary fragment of the photodissociation of dichlorodisulfane, S₂Cl₂, which is a compound featuring numerous applications (see refs [1, 2] for recent examples). While the ground state of S₂Cl has been precisely characterized in the microwave study [3], much less is known about its electronically-excited states. Thus, some of the low-lying species have been detected by various experimental techniques, including time- and state-resolved studies of the photolysis of S₂Cl₂ [4, 5], resonance Raman spectroscopy [6], and fluorescence measurements [7], but a consistent picture of the electronic excitations has not been obtained. However, an inclusion of their characteristics would be beneficial in the analysis of the dissociation channels observed in the laser absorption studies (see refs [8, 9] for details). As for the S₂Cl cation, only its ionization energy has been estimated by the mass spectrometry technique [10], and no experiments on S₂Cl anion have been reported. Also strongly limited are high-level ab initio calculations on the ground and excited electronic states of S₂Cl and its monovalent ions. They include the dated MP2 (the second-order Møller–Plesset perturbation theory) calculations on the X ²A" and 1 ²A' states of the neutral S₂Cl performed with several mid-sized basis sets [11], and the MP2/6-31G* study of the X ¹A' and 1 ³A" states of S₂Cl⁺ [10]. Consequently, a comprehensive study of the low-lying electronic states of these systems could be of interest, for example, for an elucidation of their photolysis, mainly in connection with S₂Cl₂ decomposition [9]. In this work, those states have been explored by means of the multiconfigurational-reference internally-contracted configuration interaction (MRCI) calculations [12]. Thus, the valence electronic states have been searched for by the MRCI procedure detailed in **Methods** section, and the characteristics of the

bound states thus found are presented. In particular, the proposed assignment of the \tilde{A} state of S_2Cl [6] is questioned. Additionally, the dissociation of the investigated states has been theoretically described using the CCSD(T) (coupled-cluster singles and doubles with a perturbative inclusion of connected triple excitations [13]) energies extrapolated to their complete basis set (CBS) limit, and the results have been compared to the available experimental data.

Methods

Because of the paucity of preliminary information, either experimental or theoretical, about electronic states of S_2Cl and its monovalent ions, a careful approach has been adopted in looking for the minima of the respective potential energy surfaces. Due to its well-known advantages [14], the MRCI method has been utilized in the seeking procedure, which can be briefly described as follows. The MRCI energies of the respective species (see below) have been initially calculated, without any spatial symmetry constraints, at a number of points spanning feasible regions of bond lengths and angles, and the energy landscapes have been inspected. Based on this, the grids have been narrowed in several cases, until a minimum has been approximately located. Subsequently the tight grid has been constructed (i.e., the bond length(s), r , and the bond angle, θ , have been varied with the step of 1 pm and 1° , respectively, in the vicinity of expected coordinates of the minimum), from which the equilibrium geometry and the values of vibrational frequencies, ω , have been extracted using SURVIBTM [15] (the output files can be obtained from the corresponding author upon request). In this way, the following species have been characterized: X^2A'' , $1^2A'$, $2^2A'$, $2^2A''$ states of S_2Cl ; X^1A' , $1^3A''$, $1^1A''$, $1^3A'$ states of S_2Cl^+ ; X^1A' , $1^3A'$, $1^1A''$ states of S_2Cl^- .

In all the above-mentioned calculations, the MRCI approach described in references [16] and [17] has been combined with the standard aug-cc-pVQZ basis set [18]. After a Hartree–Fock (HF) calculation, the multiconfigurational self-consistent field (MCSCF) [19, 20] step has been performed with averaging over three states from the A' and A'' irreducible representations of the C_s point group. This extent of state-averaging has been expected to be suitable for a reliable description of the lowest-lying valence states [21, 22]. The natural orbitals have been generated and the full-valence (12 active orbitals) configuration interaction subsequently performed for the electronic state of interest. For the MRCI/aug-cc-pVQZ geometries of the minima found by the searching procedure, the energies in the complete basis set limit, E_{CBS} , have been estimated. Thus, the single-point energy calculations have been carried out using an analogous MRCI protocol

adopted without the state-averaging, but with the inclusion of the multi-reference generalization of the Davidson correction [23, 24]. The family of the augmented correlation-consistent polarized-valence X -tuple basis sets with high-exponent d -functions [25], aug-cc-pV($X+d$)Z, where X is the cardinal number associated with each basis set: $X=3$ (triple- ζ , TZ), 4 (QZ), 5 (5Z), has been adopted, and E_{CBS} obtained using the mixed Gaussian/exponential form [26] (see ref. [27] for the most recent discussion of alternative extrapolation schemes)

$$E(X) = E_{CBS} + b \exp[-(X-1)] + c \exp[-(X-1)^2] \quad (1)$$

The E_{CBS} data have been employed to calculate the adiabatic relative energies, T_e , by subtracting relevant values of E_{CBS} . In some cases, the scalar relativistic effects can be important for the energetics of compounds comprising the second-row elements (see refs [28, 29]). Hence, relativistic contributions to the T_e values have been approximated by combining the standard second-order Douglas–Kroll–Hess Hamiltonian [30] with the MRCI wavefunction and the aug-cc-pV5Z Douglas–Kroll contracted basis set [31], and added to the T_e data. The adiabatic relative energies corrected for the zero-point vibrational contribution to the energy (ZPE), T_0 , have been computed as the sum of the T_e and the ΔZPE obtained using the MRCI/aug-cc-pVQZ vibrational frequencies. In addition, the dissociation behavior along both the S–Cl and S–S coordinates has been qualitatively established for all the electronic states. Thus, it has been verified that the sum of the MCSCF/aug-cc-pVQZ energies of the lowest-energy products matches the respective MCSCF/aug-cc-pVQZ energies computed at large separations between the investigated fragments.

For the two lowest electronic states of S_2Cl , S_2Cl^+ , and S_2Cl^- , the CCSD(T)/aug-cc-pVQZ gradient optimizations of the geometries have been carried out, which started from the coordinates of the corresponding MRCI/aug-cc-pVQZ minima, and was followed by the calculations of harmonic vibrational frequencies. The open-shell species, i.e., X^2A'' and $1^2A'$ states of S_2Cl , have been subjected to the coupled-cluster calculations with both the high-spin restricted-HF (RHF) and the unrestricted-HF (UHF) reference wavefunctions, described in references [32] and [33] accordingly, for comparison purposes.

In order to establish the enthalpy of the bond dissociation processes, ΔH° , of the ground states of S_2Cl , S_2Cl^+ , and S_2Cl^- , their CCSD(T)/aug-cc-pVQZ geometries have been employed to estimate the CCSD(T) E_{CBS} values of all the involved species (including pertinent diatomic molecules and atoms in their ground states) using basis sets of the same type and identical extrapolation scheme as adopted for the MRCI/CBS calculations. The ZPE values have been approximated using the CCSD(T)/aug-cc-pVQZ harmonic vibrational frequencies, while the corrections for the spin–

orbit effects (if applicable) have been taken from the literature [34, 35], and these data have been combined with the E_{CBS} to arrive at the ΔH° describing the respective bond dissociation process. The CCSD(T) estimates of the ionization potential, IP_0 , and electron affinity, EA_0 , of S_2Cl have been established in an analogous way. All the relevant absolute energies, ZPE values and spin–orbit splittings are included in the supplementary Tables S1, S2 and S3. Except for the UHF-CCSD(T) calculations specified above, which have been carried out using the default settings of Gaussian 03 [36], the Molpro 2006.1 [37] software package has been used.

Results and discussion

The neutral chlorodisulfane, S_2Cl

The characteristics of the four doublet states of S_2Cl , which have been located by the searching procedure, are summarized in Table 1 (no bound quartet states have been found). The MRCI results compare well with the available experimental data for the ground electronic state, X^2A'' . The biggest discrepancies have occurred for the S–Cl bond length and ω_3 vibrational frequency (an underestimation with respect to the experimental value by about two pm and by more than 20 cm^{-1} , respectively). An application of the CCSD(T) method, both with the RHF and UHF reference wavefunction, has led to the reduction of those

deviations (see Table 1), bringing the theoretical results to an almost perfect agreement with experiment. According to the MRCI calculations, the first excited electronic state, $1^2A'$, lies 1.34 eV above the ground state. Its CCSD(T) characteristics are closely similar to their MRCI counterparts. This is likely because the electronic configuration of the $1^2A'$ term is dominated by the one-electron transition from the highest occupied to the lowest unoccupied molecular orbital of the ground state, as specified below. From the experimental study of the photodissociation of S_2Cl_2 [6], the values of vibrational frequencies of the low-lying electronic state (denoted as \tilde{A}) have been deduced. Clearly, these data do not correspond to the calculated harmonic vibrational frequencies of the $1^2A'$ state. An effect of the anharmonic character of these vibrations has been tested at the MP2/aug-cc-pVQZ level (using the Freq=Anharmonic keyword as implemented [38] in Gaussian 03), and found to be negligible. Thus, while the harmonic frequencies are 157.4 , 518.2 and 545.5 cm^{-1} (and are only slightly underestimated with respect to their CCSD(T) counterparts from Table 1), the corrections for anharmonicity amount to -1.4 , -4.2 , -9.8 cm^{-1} accordingly. Consequently, it does not seem probable that the \tilde{A} state from ref [6] corresponds to the $1^2A'$ species. Also incompatible with the frequencies of the \tilde{A} state are the MRCI values predicted for the remaining two states, i.e., $2^2A'$ and $2^2A''$ with the adiabatic excitation energies of 2.46 and 2.91 eV, respectively (cf. Table 1).

Table 1 The characteristics of the electronic states of S_2Cl

Electronic state	T_0 [eV]	$r(SS)$ [pm]	$r(SCl)$ [pm]	θ [°]	ω_1 [cm^{-1}]	ω_2 [cm^{-1}]	ω_3 [cm^{-1}]	Dissociation products
X^2A''	0	191.87 ^a	209.00 ^a	110.4 ^a	214.5 ^a	455.3 ^a	640.7 ^a	Cl (2P_u) + S ₂ ($^3\Sigma_g^-$)
		191.25 ^b	208.29 ^b	110.0 ^b	211.6 ^b	442.7 ^b	660.3 ^b	
		191.25 ^c	208.24 ^c	109.6 ^c	216.5 ^c	446.3 ^c	663.5 ^c	
		(190.6±0.7) ^d	(207.1±0.5) ^d	(110.3±0.4) ^d	196 ^e	450 ^e	664 ^e	
$1^2A'$	1.3126 ^g 1.3747 ^h	209.83 ^a	205.07 ^a	95.6 ^a	160.7 ^a	484.8 ^a	516.0 ^a	S (3P_g) + SCl ($^2\Pi$)
		209.22 ^b	204.21 ^b	94.5 ^b	152.4 ^b	494.0 ^b	518.9 ^b	
		209.27 ^c	204.18 ^c	94.6 ^c	152.9 ^c	494.9 ^c	520.8 ^c	
					249 ^f	554 ^f	630 ^f	
$2^2A'$	2.4222 ^g	195.82 ^a	223.42 ^a	126.6 ^a	141.0 ^a	295.3 ^a	672.9 ^a	S (3P_g) + SCl ($^2\Pi$)
$2^2A''$	2.8251 ^g	208.37 ^a	222.92 ^a	106.8 ^a	121.4 ^a	222.0 ^a	487.1 ^a	Cl (2P_u) + S ₂ ($^3\Sigma_g^-$)

^a The MRCI/aug-cc-pVQZ value

^b The RHF-CCSD(T)/aug-cc-pVQZ value

^c The UHF-CCSD(T)/aug-cc-pVQZ value

^d The experimental value from ref [3]

^e The experimental value from ref [6]

^f The experimental value from ref [6] for the \tilde{A} state; see the text for details.

^g The MRCI/CBS // MRCI/aug-cc-pVQZ value combined with the MRCI/aug-cc-pVQZ correction for the ZPE and with the MRCI/aug-cc-pV5Z Douglas–Kroll estimate of scalar relativistic effects; see the text for details.

^h The RHF-CCSD(T)/CBS // RHF-CCSD(T)/aug-cc-pVQZ value

Table 2 The MRCI/aug-cc-pVQZ orbital characteristics of the electronic states of S₂Cl. The transitions are presented relative to the configuration of the ground state specified in the text

Electronic state	Configuration	Coefficients of the natural orbitals
1 ² A'	0.9063 (19a' → 6a'')	1.0026 (19a'), 1.9983 (6a'')
2 ² A'	0.8101 (6a'' → 20a') + 0.1893 (4a'' → 20a') − 0.1848 (5a'' → 6a'' 20a')	1.9369 (4a''), 1.8395 (5a''), 0.1895 (6a''), 1.0191 (20a')
2 ² A''	0.7330 (5a'' → 6a'') + 0.2805 (17a' → 20a') − 0.2222 (4a'' → 6a'') + 0.1921 (17a' 5a'' → 20a' 6a'') − 0.1555 (19a' 4a'' → 20a' 6a'')	1.9245 (17a'), 1.7420 (19a'), 0.2901 (20a'), 1.9406 (4a''), 1.8111 (5a''), 1.1682 (6a'')

The MCSCF/aug-cc-pVQZ natural orbitals have been employed to describe the electronic configuration of the X ²A'' electronic state of S₂Cl, which can be specified as follows:

$$[\text{core}](13 - 18)a'(4 - 5)a''19a'(6a'')^1(20a')^0(21a')^0$$

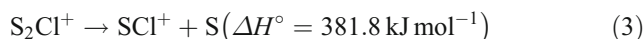
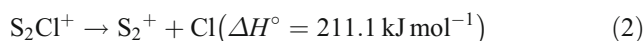
(where [core] is (1–7)a' 1a'' (8–9)a' 2a'' (10–11)a' 3a'' 12a'). Based on the MRCI/aug-cc-pVQZ calculations, the reference coefficient of this configuration is 0.8988, and the occupational numbers of the orbitals relevant for the electronic transitions amount to 1.9470, 1.9288, 1.0163, 1.0163 and 0.0785 for (17a')², (19a')², (6a'')¹, (20a')⁰ and (21a')⁰ molecular orbitals, respectively. Table 2 shows the configurations of the excited states in terms of these data. Thus, while the 1 ²A' electronic state can be approximated by a single electronic configuration, with the reference coefficient of 0.9063, the next two states are of a more complex nature. The 2 ²A' state exhibits a multireference character because of the three reference configurations in the MRCI expansion contributing more than 0.15. In the

case of the 2 ²A'' term, its strongly multireference character includes significant admixture of two biexcitations (see Table 2 for details).

It could be of interest to describe the respective dissociation channels of the electronic states of S₂Cl. As expected [39], the ground state of S₂Cl prefers the S₂ + Cl decomposition reaction (the value of ΔH°=181.9 kJ mol^{−1} has been predicted by the CCSD(T) calculations described in Methods) over the SCl + S process (ΔH°=326.2 kJ mol^{−1}). The authors of the JANAF Tables [40] have estimated, on the basis of several assumptions, the standard enthalpy of formation, Δ_fH°(0 K), of S₂Cl to be 79.5±8.4 kJ mol^{−1}. In reasonable agreement with this value is the result obtained by combining the computed CCSD(T) data with the tabulated Δ_fH°(0 K) for S₂ [35], i.e., Δ_fH°(0)=65.6 kJ mol^{−1}. As for the excited electronic states of S₂Cl, it has been revealed by the MCSCF/aug-cc-pVQZ method that they preferentially decompose into the products listed in Table 1, all of them being the ground states of the corresponding species.

The chlorodisulfane cation, S₂Cl⁺

Table 3 summarizes the computational results, which describe the only four stable valence states of S₂Cl⁺ found by the MRCI procedure. All the excited electronic states have been predicted to lie within two eV from the ground state (see Table 3). Eberhard et al. have obtained the value of the ionization potential of S₂Cl⁺, IP₀=9.04±0.03 eV, from the photoionization-efficiency spectra, and reported its G2 [41] counterpart to be 8.93 eV [10]. The CCSD(T)/CBS estimate of 9.069 eV agrees with experiment within its error bars. It is expected that the CCSD(T) values of the enthalpies of possible decomposition reactions are also reliable:

**Table 3** The characteristics of the electronic states of S₂Cl⁺

Electronic state	T ₀ [eV]	r(SS) [pm]	r(SCl) [pm]	θ [°]	ω ₁ [cm ^{−1}]	ω ₂ [cm ^{−1}]	ω ₃ [cm ^{−1}]	Dissociation products
X ¹ A'	0	186.36 ^a 186.00 ^b	199.00 ^a 198.54 ^b	113.7 ^a 113.2 ^b	248.2 ^a 246.2 ^b	531.3 ^a 534.0 ^b	704.1 ^a 726.6 ^b	Cl (² P _u) + S ₂ ⁺ (² Π _g)
1 ³ A''	1.0655 ^c 1.0668 ^d	199.13 ^a 198.50 ^b	199.66 ^a 199.46 ^b	100.6 ^a 99.2 ^b	150.9 ^a 150.0 ^b	530.5 ^a 528.7 ^b	554.6 ^a 575.5 ^b	S (³ P _g) + SCl ⁺ (³ Σ [−])
1 ¹ A''	1.4927 ^a	200.22 ^a	198.93 ^a	99.8 ^a	153.3 ^a	495.5 ^a	554.9 ^a	S (³ P _g) + SCl ⁺ (³ Σ [−])
1 ³ A'	1.9084 ^a	208.04 ^a	197.07 ^a	106.9 ^a	218.1 ^a	616.4 ^a	694.4 ^a	S (³ P _g) + SCl ⁺ (³ Σ [−])

^a The MRCI/aug-cc-pVQZ value

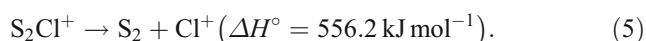
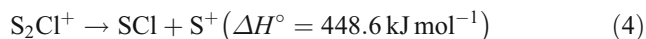
^b The RHF-CCSD(T)/aug-cc-pVQZ value

^c The MRCI/CBS // MRCI/aug-cc-pVQZ value combined with the MRCI/aug-cc-pVQZ correction for the ZPE and with the MRCI/aug-cc-pV5Z Douglas–Kroll estimate of scalar relativistic effects; see the text for details.

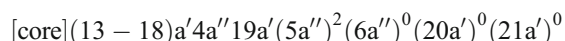
^d The RHF-CCSD(T)/CBS // RHF-CCSD(T)/aug-cc-pVQZ value

Table 4 The MRCI/aug-cc-pVQZ orbital characteristics of the electronic states of S_2Cl^+ . The transitions are presented relative to the configuration of the ground state specified in the text

Electronic state	Configuration	Coefficients of the natural orbitals
$^3A''$	0.9005 (19a' → 6a'')	0.9977 (19a'), 1.0180 (6a'')
$^1A''$	0.8977 (19a' → 6a'')	0.9997 (19a'), 1.0167 (6a'')
$^3A'$	0.8993 (5a'' → 6a'')	1.0160 (5a''), 0.9921 (6a'')



Clearly, the dissociation of the ground electronic state of S_2Cl^+ would preferentially proceed according to the reaction (2). In contrast, the excited states have been found to dissociate into the ground electronic states of SCl^+ and of the sulfur atom. In analogy with the first excited state of S_2Cl , the MRCI and CCSD(T) treatments of the $1^3A''$ term of S_2Cl^+ have yielded almost the same geometries and the ω_1 and ω_2 vibrational frequencies, and comparable values of ω_3 and T_0 (see Table 3). This is not unexpected because of the single-reference character of these species, which follows from a comparison of Tables 2 and 4. Thus, in the case of S_2Cl^+ , the ground state configuration



([core] stands for (1–7)a' 1a'' 8a' 2a'' (9–10)a' 3a'' (11–12)a') has the MRCI/aug-cc-pVQZ reference coefficient of 0.8828 and the occupational numbers 1.9259, 1.8734 and 0.1337 accordingly for the $(19a')^2$, $(5a'')^2$ and $(6a'')^0$ molecular orbitals, and the electronic transitions are presented with respect to it in Table 4. An inspection of this table reveals that all the excited states of S_2Cl^+ are dominated by monoexcitations.

Table 5 The characteristics of the electronic states of S_2Cl^-

Electronic state	T_0 [eV]	$r(SS)$ [pm]	$r(SCl)$ [pm]	θ [°]	ω_1 [cm ⁻¹]	ω_2 [cm ⁻¹]	ω_3 [cm ⁻¹]	Dissociation products
X^1A'	0	199.33 ^a 198.89 ^b	226.51 ^a 223.42 ^b	111.8 ^a 110.1 ^b	151.1 ^a 160.7 ^b	294.2 ^a 306.5 ^b	563.9 ^a 579.6 ^b	$Cl^- (^1S_g) + S_2 (a^1\Delta_g)$
$^3A'$	1.6235 ^c 1.6097 ^d	207.74 ^a 207.40 ^b	276.19 ^a 277.15 ^b	67.9 ^a 68.0 ^b	174.3 ^a 166.6 ^b	217.3 ^a 207.4 ^b	514.3 ^a 532.4 ^b	$Cl (^2P_u) + S_2^- (^2\Pi_g)$
$^1A''$	2.4769 ^c	195.02 ^a	286.77 ^a	102.0 ^a	97.5 ^a	203.7 ^a	588.5 ^a	$Cl^- (^1S_g) + S_2 (a^1\Delta_g)$

^a The MRCI/aug-cc-pVQZ value

^b The RHF-CCSD(T)/aug-cc-pVQZ value

^c The MRCI/CBS // MRCI/aug-cc-pVQZ value combined with the MRCI/aug-cc-pVQZ correction for the ZPE and with the MRCI/aug-cc-pV5Z Douglas–Kroll estimate of scalar relativistic effects; see the text for details.

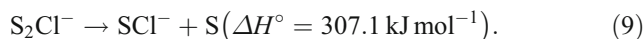
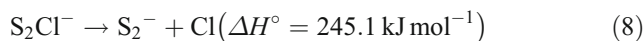
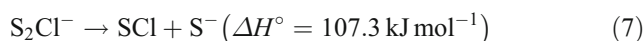
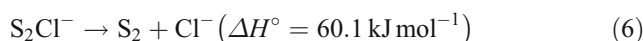
^d The RHF-CCSD(T)/CBS // RHF-CCSD(T)/aug-cc-pVQZ value

Table 6 The MRCI/aug-cc-pVQZ orbital characteristics of the electronic states of S_2Cl^- . The transitions are presented relative to the configuration of the ground state specified in the text

Electronic state	Configuration	Coefficients of the natural orbitals
$^3A'$	0.9069 (19a' → 20a')	1.0046 (19a'), 1.0045 (20a')
$^1A''$	0.9058 (6a'' → 20a')	1.0327 (6a''), 1.0304 (20a')

The chlorodisulfane anion, S_2Cl^-

The MRCI and CCSD(T) computational protocols have been also applied to the lowest-lying electronic states of S_2Cl^- . In addition to the data gathered in Table 5, the CCSD(T)/CBS estimate of the electron affinity of S_2Cl , $EA_0 = -2.352$ eV, has been obtained. The enthalpies of the S_2Cl^- decomposition reactions, which have been calculated with respect to the ground electronic states of the products, are as follows:



However, the correct dissociation limit needs to be considered for the reaction (6), i.e., $Cl^- (^1S_g) + S_2 (a^1\Delta_g)$. Consequently, the ΔH° value should be increased by the excitation energy of the $a^1\Delta_g$ state of S_2 with respect to the $^3\Sigma_g^-$ ground state ($T_0 = 4394.25$ cm⁻¹ [42]), leading to the dissociation energy of 112.7 kJ mol⁻¹. Interestingly, this value then surpasses the ΔH° of the reaction (7), indicating the possibility of

two competing decomposition channels. The $1^1A''$ excited state has been predicted to reach in the dissociation limit the $a^1\Delta_g$ state of S_2 and the chlorine anion, while the dissociation products of the $1^3A'$ excited state have been identified as the ground states of S_2^- and the chlorine atom (see Table 5). The electronic configurations of the $1^1A''$ and $1^3A'$ terms are specified in Table 6 relative to the configuration of the X^1A' state of S_2Cl^- :

$$[\text{core}](13 - 17)a'4a''18a'5a''19a'6a''(20a')^0(21a')^0$$

where [core] denotes $(1-8)a' 1a'' 9a' 2a'' (10-12)a' 3a''$, the MRCI/aug-cc-pVQZ reference coefficient is 0.8989, and the occupational numbers are 1.9227, 0.0886 and 1.9592 for the $(19a')^2$, $(20a')^0$ and $(6a'')^2$ molecular orbitals, respectively.

Conclusions

The MRCI and CCSD(T) methods have been combined with large correlation-consistent basis sets to reliably describe the structure and energetics of the low-lying electronic states of S_2Cl and its monovalent ions. As for S_2Cl , the characteristics of its ground state have been obtained in excellent agreement with experiment, however, it has not been possible to assign the measured vibrational frequencies of the \tilde{A} state [6] to any of the electronic states. According to the MRCI calculations, the $2^2A'$ and $2^2A''$ terms of S_2Cl feature a strongly multi-reference character, while all the excited states of S_2Cl^+ and S_2Cl^- are dominated by the single replacements from the reference determinants. Considering the level of accuracy of the adopted approach to the thermochemical calculations, which is less demanding than the strategies most recently discussed in ref. [43], and taking into account the assumptions made in estimating the dissociation energies in ref. [40], a good agreement between the computed and tabulated enthalpy of formation of S_2Cl has been obtained. Significantly, the value of the ionization potential of S_2Cl has been found within the error bars of the measurements [10], and its electron affinity, $EA_0 = -2.352$ eV, has been predicted for the first time. This value is comparatively large, despite that the S_2Cl^- system can be considered as rather weakly bound. The dissociation pathways of all the electronic states have been established.

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References

- Berger R, Gottselig M, Quack M et al. (2001) Parity violation dominates the dynamics of chirality in dichlorodisulfane. *Angew Chem Int Ed* 40:9195–9198
- da Silva BV (2008) Disulfur dichloride (S_2Cl_2). *Synlett* 8:1265–1266
- Fujitake M, Hirota E (1994) The microwave spectrum of the ClS_2 radical. *Can J Chem* 70:1043–1050
- Park J, Lee Y, Flynn GW (1991) Tunable diode laser probe of chlorine atoms produced from the photodissociation of a number of molecular precursors. *Chem Phys Lett* 186:441–449
- Speth RS, Niemann R, Tiemann E (1998) Photodissociation of S_2Cl_2 : state-specific detection of atomic and molecular sulphur. *Chem Phys* 229:309–323
- Chiu L, Chang H (1994) Observation of photodissociation of S_2Cl_2 and resonance Raman and fluorescence spectra of S_2Cl under 514.5 nm radiation. *Spectrochim Acta* 50A:2239–2248
- Chiu CL, Chang H (1995) Fluorescence spectra of S_2Cl excited with laser radiation at 488 nm. *J Chin Chem Soc* 42:19–24
- Lee YR, Chiu CL, Lin SM (1993) Photodissociation of S_2Cl_2 at 308 nm by translational spectroscopy. *Chem Phys Lett* 216:209–214
- Einfeld TS, Maul C, Gericke KH, Chichinin A (2002) Competing dissociation channels in the photolysis of S_2Cl_2 at 235 nm. *J Chem Phys* 117:4214–4219
- Eberhard J, Chen WC, Yu CH, Lee YP, Cheng BM (1998) Photoionization spectra and ionization energies of HS_2Cl , $HSSSH$, $SSCl$, and $HSSCl$ formed in the reaction system $Cl/Cl_2/H_2S$. *J Chem Phys* 108:6197–6204
- Zhuo Q, Clouthier DJ, Goddard JD (1994) Ab initio predictions of the structures and spectra of some simple thiosulfeno (XS_2) free radicals. *J Chem Phys* 100:2924–2931
- Knowles PJ, Werner HJ (1992) Internally contracted multiconfiguration-reference configuration-interaction calculations for excited states. *Theor Chim Acta* 84:95–103
- Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) A 5th order comparison of electron correlation theories. *Chem Phys Lett* 157:479–483
- Werner HJ (1987) Matrix-formulated direct multiconfiguration self-consistent field and multiconfiguration reference configuration-interaction methods. *Adv Chem Phys* 69:1–62
- Ermiler WC, Hsieh HC, Harding LB (1988) Polyatomic surface fitting, vibrational–rotational analysis, expectation values and intensity program. *Comput Phys Commun* 51:257–284
- Werner HJ, Knowles PJ (1988) An efficient internally contracted multiconfiguration reference configuration-interaction method. *J Chem Phys* 89:5803–5814
- Knowles PJ, Werner HJ (1988) An efficient method for the evaluation of coupling-coefficients in configuration-interaction calculations. *Chem Phys Lett* 145:514–522
- Kendall RA, Dunning TH Jr, Harrison RJ (1992) Electron-affinities of the 1st-row atoms revisited – systematic basis-sets and wave-functions. *J Chem Phys* 96:6796–6806
- Werner HJ, Knowles PJ (1985) A 2nd order multiconfiguration SCF procedure with optimum convergence. *J Chem Phys* 82:5053–5063
- Knowles PJ, Werner HJ (1985) An efficient 2nd-order MC SCF method for long configuration expansions. *Chem Phys Lett* 115:259–267
- Czernek J, Živný O (2011) Low-lying electronic states of SF_2 and its ions as studied by the MRCI technique. *Chem Phys* 344:142–146
- Czernek J, Živný O (2011) The MRCI studies of low-lying excited states of Al_3 and Al_3^- . *Chem Phys Lett* 512:40–43
- Langhoff SR, Davidson ER (1974) Configuration interaction calculations on nitrogen molecule. *Int J Quantum Chem* 8:61–72
- Butscher W, Shih SK, Buenker RJ, Peyerimhoff SD (1977) Configuration interaction calculations for N_2 molecule and its 3 lowest dissociation limits. *Chem Phys Lett* 52:457–462
- Dunning TH Jr, Peterson KA, Wilson AK (2001) Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J Chem Phys* 114:9244–9253

26. Peterson KA, Woon DA, Dunning TH Jr (1994) Benchmark calculations with correlated wave-functions. *J Chem Phys* 100:7410–7415
27. Feller D, Peterson KA, Hill JG (2011) On the effectiveness of CCSD(T) complete basis set extrapolations for atomization energies. *J Chem Phys* 135: Art. No. 044102
28. Mok DKW, Chau FT, Lee EPF, Dyke JM (2006) Ab initio calculations of SCl_2 and low-lying cationic states of SCl_2^+ : Franck–Condon simulation of the UV photoelectron spectrum of SCl_2 . *J Chem Phys* 125: 104303
29. Puzzarini C (2011) Accurate thermochemistry and spectroscopy of the oxygen-protonated sulfur dioxide isomers. *Phys Chem Chem Phys* 13:21319–21327
30. Wolf A, Reiher M, Hess BA (2002) The generalized Douglas–Kroll approximation. *J Chem Phys* 117:9215–9226
31. de Jong WA, Harrison RJ, Dixon DA (2001) Parallel Douglas–Kroll energy and gradients in NWChem: estimating scalar relativistic effects using Douglas–Kroll contracted basis sets. *J Chem Phys* 114:48–53
32. Watts JD, Gauss J, Bartlett RJ (1993) Coupled-cluster methods with noniterative triplet excitations for restricted open-shell Hartree–Fock and other general single determinant reference wavefunctions – energies and analytical gradients. *J Chem Phys* 98:8718–8733
33. Pople JA, Krishnan R, Schlegel HB, Binkley JS (1978) Electron correlation theories and their application to study of simple reaction potential surfaces. *Int J Quantum Chem* 14:545–560
34. Ralchenko Y, Kramida A, Reader J and NIST ASD Team (2011) NIST Atomic Spectra Database (version 4.1). Available online at <http://physics.nist.gov/asd>
35. Huber KP, Herzberg G. Constants of diatomic molecules (2011; data prepared by Gallagher JW, Johnson R D III). NIST Chemistry Webbook, NIST Standard Reference Database Number 69. Available online at <http://webbook.nist.gov>
36. Frisch MJ, Trucks GW, Schlegel HB et al. (2004) Gaussian 03, Revision C02. Gaussian Inc, Wallingford
37. Werner HJ, Knowles PJ, Lindh R et al. (2006) MOLPRO, version 2006.1. A package of ab initio programs, see <http://www.molpro.net>
38. Barone V (2004) Vibrational zero-point energies and thermodynamic functions beyond the harmonic approximation. *J Chem Phys* 120:3059–3065
39. Benson SW (1978) Thermochemistry and kinetics of sulfur-containing molecules and radicals. *Chem Rev* 78:23–35
40. Chase MW Jr (1998) NIST-JANAF Thermochemical Tables, Fourth Edition. *J Phys Chem Ref Data Monogr* 9:1–1951
41. Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) Gaussian-2 theory for molecular-energies of 1st-row and 2nd-row compounds. *J Chem Phys* 94:7221–7230
42. Setzer KD, Kalb M, Fink EH (2003) The $a^1\Delta_g \rightarrow ^3\Sigma_g^-$ magnetic dipole transition of S_2 . *J Mol Spectrosc* 221:127–130
43. Karton A, Daon S, Martin JML (2011) W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data. *Chem Phys Lett* 510:165–178