

Theoretical Investigation of the Electronic Structure of the Strontium Mono-Sulfide Molecule SrS Using the *ab initio* Calculation Method

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Abstract

The ground state and 23 other low-lying singlet and triplet electronic states of the strontium mono-sulfide molecule SrS, in the $^{2s+1}\Lambda^{\pm}$ representation, have been examined by *ab initio* calculations using the computational chemistry software MOLPRO and the graphical user interface GABEDIT. The potential energy curves, in terms of the internuclear distance R, resulted from the complete active space self-consistent field (CASSCF) and multi-reference doubly and singly configuration interaction (MRDSCI) with Davidson correction (+Q) calculations. The permanent dipole moments (μ) and the spectroscopic constants (T_e : the electronic energy with respect to the ground state, ω_e : the harmonic frequency, R_e : the equilibrium internuclear distance, B_e : the rotational constant, D_e : the equilibrium dissociation energy) have been investigated. The results of this work are in good agreement with the results available in literature. Moreover, for the first time, it was possible to study 20 new singlet and triplet electronic states of SrS molecule.

Keywords: strontium mono-sulfide, computational chemistry, *ab initio* calculation, potential energy curves, permanent dipole moment curves, spectroscopic constants

1. Introduction

In many areas of chemistry, the compound SrS, as all metal sulfides, is of great importance regarding the nature of the metal-sulfur bond. Corrosion processes, high temperature chemistry, and chemical vapor deposition are some examples of the significance of metal sulfide compounds (Halfen, Apponi, Thompsen, & Ziurys, 2001) (Bradley, 1989). Metal sulfides also play a role in biochemistry (Janczyk & Ziurys, 2006) where they are considered as sulfur-donating ligands in protein related reactions (Holm, Kennepohl & Solomon, 1996) (Halfen, Apponi, Thompsen, & Ziurys, 2001). Moreover, alkaline earth sulfide applications also exist in astrophysics (Takano, Yamamoto, & Saito, 1989) (Janczyk & Ziurys, 2006). Therefore, scientists are often interested in studying their properties.

Many alkaline-earth metal sulfides have been investigated experimentally and theoretically. However, studies conducted on the SrS molecule, unfortunately, remained few and constricted to only some low-lying electronic states (Marcano & Barrow, 1970) (Huber & Herzberg, 1979). For instance, a laser spectroscopy experiment was conducted, in 1988, on strontium sulfide, SrS, in order to obtain molecular constants, such as vibrational constants, rotational constants and bond lengths, with high accuracy and precision. The results were limited to 2 electronic states only, the ground state $X^1\Sigma^+$ and the first excited state $(2)^1\Sigma^+$ (Pianalto, Brazier, Obrien, & Bernath, 1988). Another experimental study, in 2001, allowed the recording of the bond length of SrS, for state $X^1\Sigma^+$, using millimeter/submillimeter-wave direct absorption methods (Halfen, Apponi, Thompsen, & Ziurys, 2001). Later, in 2010, experimental recordings were done on 4 isotopes of strontium mono-sulfide and the spectroscopic constants of the ground state $X^1\Sigma^+$ were obtained (Etchison & Cooke, 2010). Theoretically, this molecule has been studied by Partridge *et al.* using *ab initio* calculations. The study resulted in spectroscopic constants computed by 5 different calculation techniques (CASSCF: complete active space self-consistent field, CCI: contracted configuration interaction, CCI(4s4p): CCI with core correlation, MRCI: multi-reference configuration interaction, MRCI+Core: MRCI with core correlation) for three low-lying SrS electronic states: $X^1\Sigma^+$, $(1)^3\Pi$, and $(1)^1\Pi$ (Partridge, Langhoff, & Bauschlicher, 1988).

In the present work, the investigation of the ground state and several low-lying singlet and triplet electronic states of SrS, in the $^{2s+1}\Lambda^{\pm}$ representation, is done using multi-reference configuration interaction (MRCI with

Davidson correction) according to the *ab initio* computational method. Accordingly, the potential energy curves (PECs) of 24 electronic states and the permanent dipole moment curves (DMCs) of 19 electronic states are presented. The corresponding spectroscopic constants, such as the electronic energy with respect to the ground state (T_e), the harmonic frequency (ω_e), the internuclear distance at equilibrium (R_e), the rotational constant (B_e) and the dissociation energy (D_e), are also computed for 19 electronic states. Out of the 24 low-lying electronic states that are demonstrated in the current work, 20 new electronic states are studied here for the first time.

2. Computational Approach

Taking advantage of the graphical user interface GABEDIT (Allouche, 2010), the computational chemistry program MOLPRO (Werner, Knowles, Knizia, Manby, & Schütz, 2011) has been used in the current study to apply *ab initio* techniques to the strontium mono-sulfide compound. Using the state averaged complete active space self-consistent field (CASSCF) approach, the low-lying singlet and triplet electronic states of the diatomic molecule SrS have been studied by the method of multi-reference doubly and singly configuration interaction (MRDSCI) with Davidson correction (+Q). The strontium atom Sr, in its neutral state with 38 electrons, is treated with the energy-consistent effective core potential ECP28MWB basis (Kaupp, Schleyer, Stoll & Preuss, 1991), for *s*, *p* and *d* functions ($6s, 6p, 5d$)/[$4s, 4p, 2d$], where 28 electrons are considered in the core and the remaining 10 electrons are valence. As for the neutral sulfur atom S, its 16 electrons are distributed into 10 core electrons and 6 valence electrons using the ECP10MWB basis set (Bergner, Dolg, Kuechle, Stoll & Preuss, 1993) for *s* and *p* functions ($4s, 5p$)/[$2s, 3p$]. Both Wood-Boring (WB) effective core potential basis sets, ECP28MWB and ECP10MWB, represent a quasi-relativistic theoretical level of reference. Considering strontium mono-sulfide's 54 electrons, of which 38 electrons are for Sr and 16 electrons are for S, 38 electrons are made to belong to the core of the molecule (28 electrons from Sr and 10 electrons from S) and 16 electrons (the 10 valence electrons of Sr and the 6 valence electrons of S) are kept outside this core. The wave functions of these 16 out-of-core electrons are specified using 19 molecular active orbitals formed on $4s, 4p, 4d, 5s, 5p$ and $6s$ of strontium and $3s, 3p$ and $4s$ of sulfur. The later calculations are done by freezing 10 electrons in the $4s$ and $4p$ orbitals of Sr and in the $3s$ orbital of S by keeping them doubly occupied, consequently leaving the explicit treatment to 6 valence electrons. As a result, the orbitals contained in the active space are 6σ (Sr: $5s, 4d_{\sigma}, 5p_{\sigma}, 6s$; S: $3p_{\sigma}, 4s$), 3π (Sr: $4d_{\pm 1}, 5p_{\pm 1}$; S: $3p_{\pm 1}$) and 1δ (Sr: $4d_{\pm 2}$) distributed into the irreducible representations a_1, b_1, b_2 and a_2 as $3a_1, 1b_1, 1b_2$ and $0a_2$, denoted by [3, 1, 1, 0] in the C_{2v} point group symmetry.

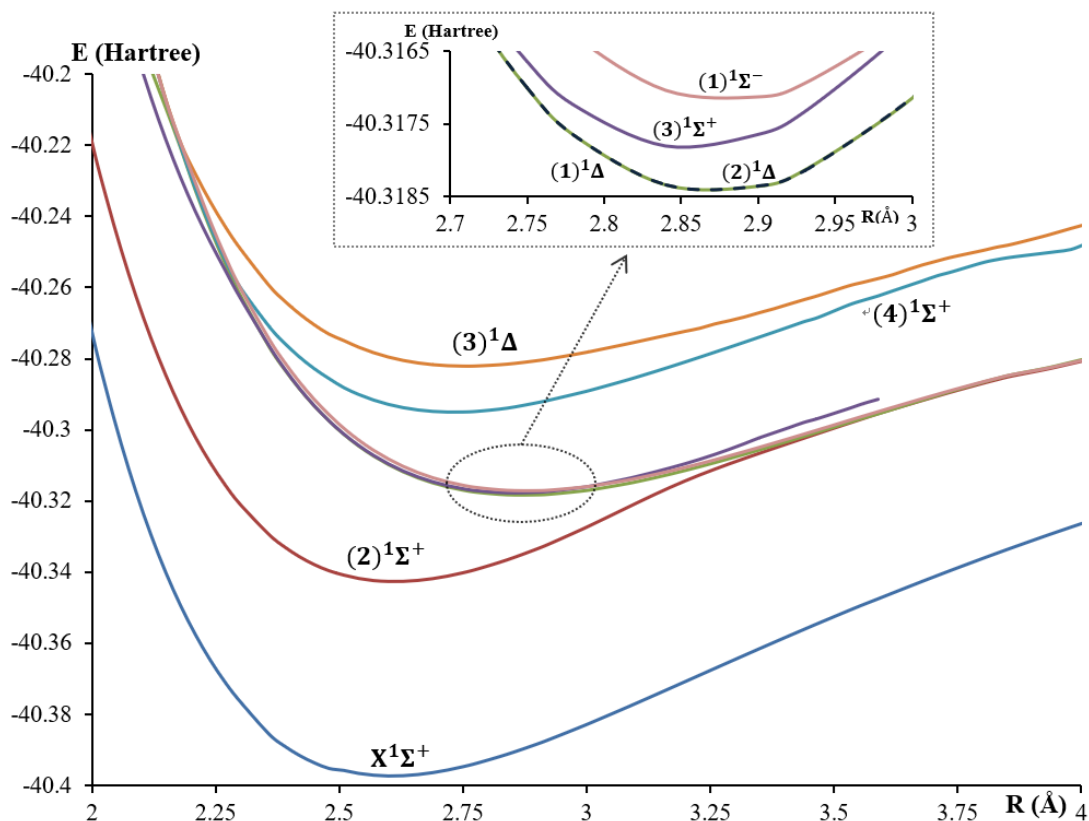


Figure 1. PECs of the singlet Σ and Δ electronic states of SrS

3. Results and Discussion

3.1 Potential Energy Curves and Spectroscopic Constants

In the range $2 \text{ \AA} \leq R \leq 4.01 \text{ \AA}$, the potential energy curves (PECs), as a function of R , for the 24 singlet and triplet low-lying electronic states of the SrS molecule, in the $^{2s+1}\Lambda^\pm$ representation, have been calculated and presented for 77 internuclear distances (Figs. 1-5).

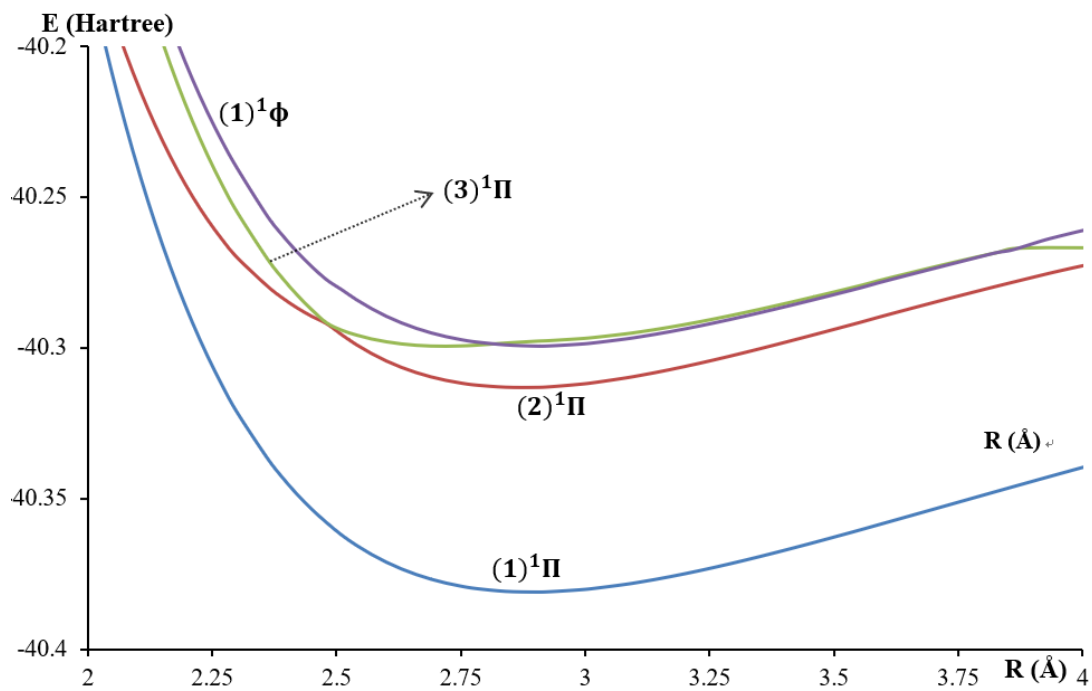


Figure 2. PECs of the singlet Π and Φ electronic states of SrS

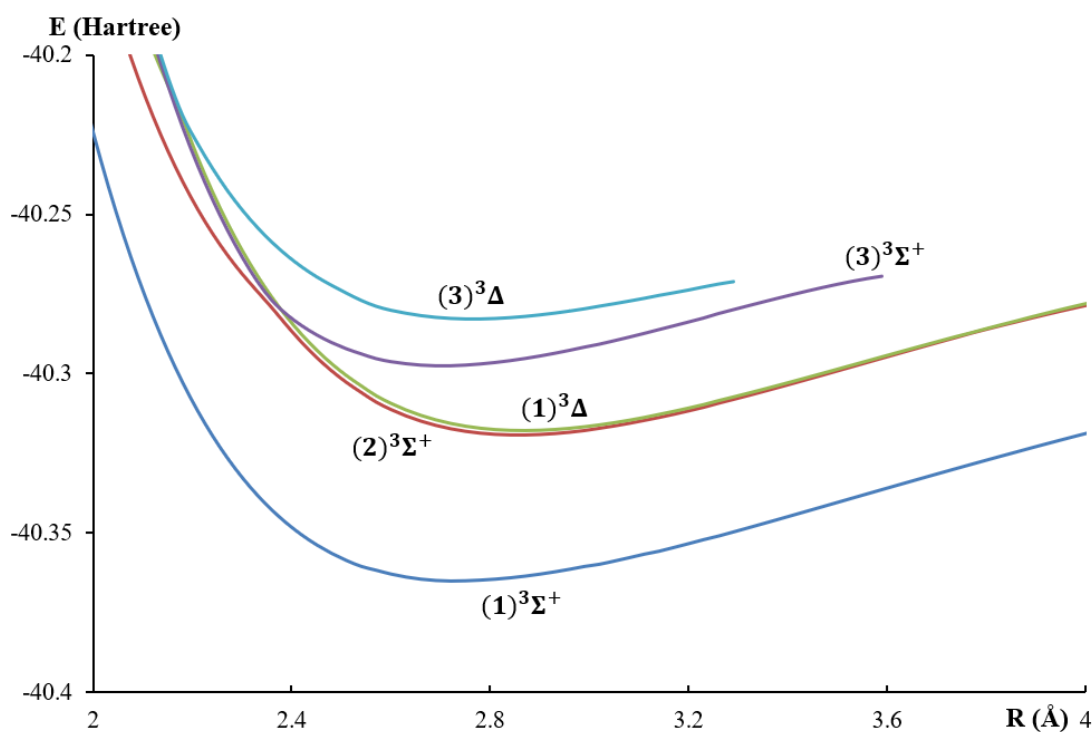


Figure 3. PECs of the triplet Σ^+ and some triplet Δ electronic states of SrS

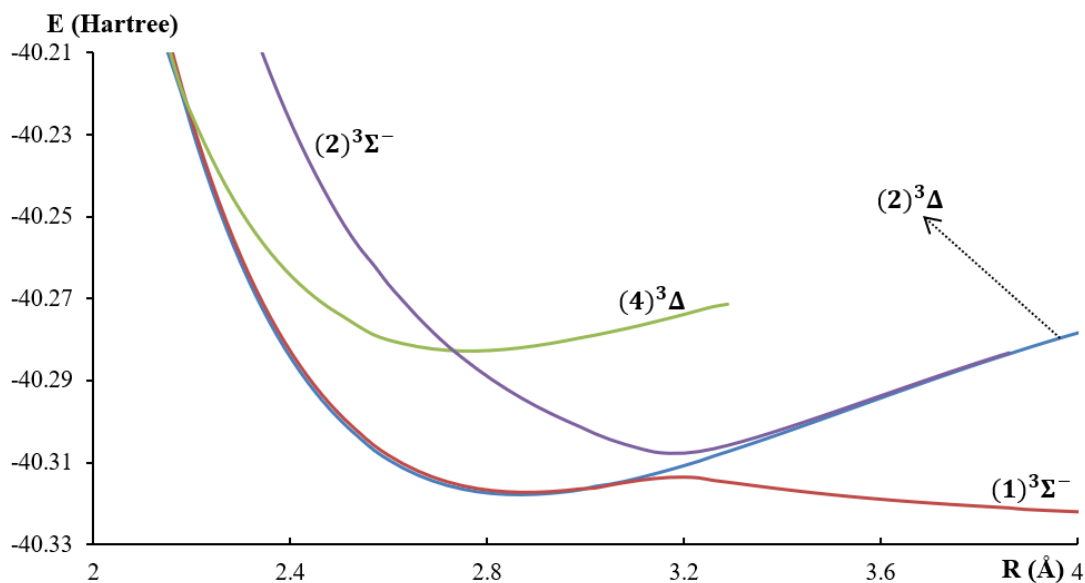


Figure 4. PECs of some triplet Δ and Σ^- electronic states of SrS

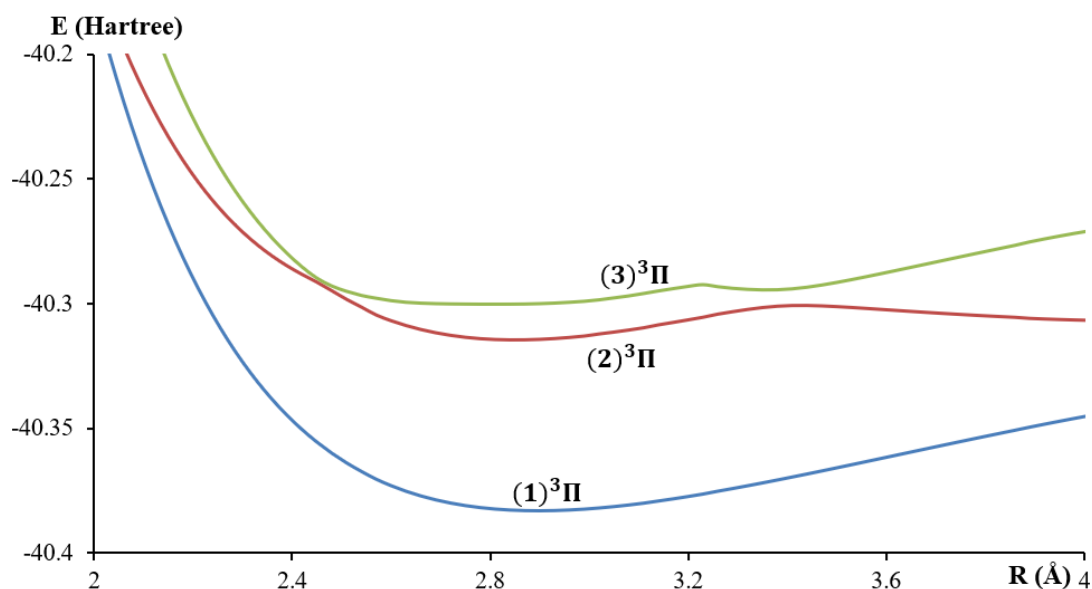


Figure 5. PECs of the triplet Π electronic states of SrS

By fitting the potential energy values into a polynomial in R around the internuclear distance at equilibrium, spectroscopic constants of SrS have been computed. The constants T_e (the electronic energy with respect to the ground state), ω_e (the harmonic vibrational frequency), R_e (the equilibrium internuclear distance), B_e (the rotational constant) and D_e (the equilibrium dissociation energy) have been obtained for 19 singlet and triplet SrS electronic states (Table 1). The spectroscopic constants of few other electronic states have not been calculated since the minima of their potential energy curves exist near locations of crossing or avoided-crossing between two states.

In order to study the effect of decreasing the core orbitals of the SrS molecule during the MRCI calculations, another MRDSCI computational trial has been applied to 2 states of SrS (using the same Sr and S basis sets mentioned earlier) by removing 1 of the closed-shell s orbitals from the core orbitals and the corresponding spectroscopic constants have been calculated (Table 1^b). One can notice that this trial has led to promising results in comparison to previous experimental studies.

Table 1. Calculated spectroscopic constants for the singlet and triplet electronic states of the SrS molecule.

State	T_e (cm ⁻¹)	r_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	$10^8 D_e$ (cm ⁻¹)
$X^1\Sigma^+$	0 ^a	2.607 ^a	269.3049 ^a	0.105544 ^a	6.54 ^a
	0 ^b	2.589 ^b	312.0721 ^b	0.107188 ^b	5.01 ^b
	0 ^c	2.440 ^c	388.38 ^c	0.12072 ^c	4.75 ^c
	0 ^{d,1}	2.484 ^{d,1}	390 ^{d,1}		
	0 ^{d,2}	2.507 ^{d,2}	363 ^{d,2}		
	0 ^{d,3}	2.458 ^{d,3}	377 ^{d,3}		
	0 ^e	2.439 ^e	388.2643 ^e	0.120803 ^e	4.87 ^e
	0 ^f	2.441 ^f		0.120797 ^f	4.67 ^f
	0 ^{g,1}	2.439 ^{g,1}		0.120793 ^{g,1}	4.67 ^{g,1}
	0 ^{g,2}	2.439 ^{g,2}		0.121162 ^{g,2}	4.70 ^{g,2}
0 ^{g,3}	2.439 ^{g,3}		0.121541 ^{g,3}	4.73 ^{g,3}	
0 ^{g,4}	2.439 ^{g,4}		0.115589 ^{g,4}	4.28 ^{g,4}	
(1) ¹ Π	3522.03 ^a	2.891 ^a	231.7985 ^a	0.085891 ^a	4.71 ^a
	7179 ^{d,1}	2.751 ^{d,1}	273 ^{d,1}		
(1) ³ Π	6548.01 ^a	2.897 ^a	227.2335 ^a	0.085535 ^a	4.84 ^a
	9881 ^{d,1}	2.788 ^{d,1}	273 ^{d,1}		
	5503 ^{d,2}	2.807 ^{d,2}	262 ^{d,2}		
	5823 ^{d,3}	2.749 ^{d,3}	270 ^{d,3}		
	6550 ^{d,4}	2.808 ^{d,4}	258 ^{d,4}		
(1) ³ Σ ⁺	10494.48 ^a	2.733 ^a	256.8097 ^a	0.096122 ^a	5.37 ^a
(2) ¹ Σ ⁺	11937.50 ^a	2.613 ^a	304.3698 ^a	0.105109 ^a	5.01 ^a
	11753.24 ^b	2.613 ^b	305.7439 ^b	0.105091 ^b	5.04 ^b
	13932.70 ^c	2.511 ^c	339.1454 ^c	0.113989 ^c	6.16 ^c
(1) ¹ Δ	17262.06 ^a	2.871 ^a	234.3688 ^a	0.087133 ^a	4.81 ^a
(2) ¹ Δ	17262.38 ^a	2.870 ^a	234.3205 ^a	0.087134 ^a	4.82 ^a
(3) ¹ Σ ⁺	17395.79 ^a	2.857 ^a	244.7969 ^a	0.087986 ^a	4.54 ^a
(1) ¹ Σ ⁻	17540.41 ^a	2.878 ^a	232.2611 ^a	0.086709 ^a	4.83 ^a
(2) ¹ Π	18444.97 ^a	2.873 ^a	234.6076 ^a	0.086972 ^a	4.78 ^a
(2) ³ Σ ⁺	20609.10 ^a	2.858 ^a	238.2755 ^a	0.087915 ^a	4.79 ^a
(1) ³ Σ ⁻	20862.41 ^a	2.868 ^a	236.8683 ^a	0.087246 ^a	4.75 ^a
(1) ³ Δ	20862.98 ^a	2.867 ^a	236.7714 ^a	0.087358 ^a	4.75 ^a
(2) ³ Δ	21031.22 ^a	2.879 ^a	224.0832 ^a	0.086647 ^a	5.13 ^a
(2) ³ Π	21635.23 ^a	2.850 ^a	249.6852 ^a	0.088391 ^a	4.40 ^a
(4) ¹ Σ ⁺	22386.03 ^a	2.736 ^a	260.7516 ^a	0.095836 ^a	5.17 ^a
(3) ¹ Δ	25241.23 ^a	2.756 ^a	236.7732 ^a	0.094536 ^a	6.02 ^a
(3) ³ Σ ⁺	25323.85 ^a	2.700 ^a	266.1296 ^a	0.098487 ^a	5.36 ^a
(3) ³ Δ	28562.08 ^a	2.767 ^a	208.6114 ^a	0.093624 ^a	7.76 ^a

^aPresent work with all core orbitals during the CASSCF/MRDSCI calculation.

^bPresent work by decreasing the core orbitals by 1 during the CASSCF/MRDSCI calculation (for 2 states only).

^cExperimental work by M. Marcano and R. F. Barrow (Marcano & Barrow, 1970).

^dTheoretical work by Partridge *et al.* using 5 methods (d1: CASSCF, d2: CCI, d3: CCI (4s4p), d4: MRCI, d5: MRCI+Core) (Partridge, Langhoff, & Bauschlicher, 1988).

^eExperimental work by Pianalto *et al.* (Pianalto, Brazier, O'Brien, & Bernath, 1988).

^fExperimental work by Halfen *et al.* (Halfen, Apponi, Thompsen, & Ziurys, 2001).

^gExperimental work by K. C. Etchison for 4 SrS isotopes (g1:⁸⁸Sr³²S, g2:⁸⁷Sr³²S, g3:⁸⁶Sr³²S, g4:⁸⁸Sr³⁴S) (Etchison & Cooke, 2010).

In Table 1, the obtained results are compared to the results of the experimental and theoretical studies found in earlier literature (Marcano & Barrow, 1970) (Partridge, Langhoff, & Bauschlicher, 1988) (Pianalto, Brazier,

Obrien, & Bernath, 1988) (Halfen, Apponi, Thompsen, & Ziurys, 2001) (Etchison & Cooke, 2010). The spectroscopic constants in our study are generally in good agreement with the previous theoretical and experimental work. For instance, it is noticeable that the constants calculated here are very close to the CCI, MRCI and MRCI+Core theoretical outcomes of Partridge *et al.* (Table 1/^{d2, d4 and d5}) (Partridge, Langhoff, & Bauschlicher, 1988). As for the T_e values of the states $(1)^1\Pi$ and $(1)^3\Pi$ resulting from the CASSCF method used by Partridge *et al.*, they are remarkably higher than the results in the present study (Table 1/^{d1}). This can be explained by the fact that the CASSCF method can be considered as a full CI computation in a restricted configurational space, which is sometimes problematic during the process of selecting configurations, whereas a multi-reference CI tends to result in more optimized calculations (Kohanoff, 2006).

Some sites of crossing and avoided-crossing between different electronic states of strontium mono-sulfide appear in the PECs (Fig. 1-5). For example, in Figure 1, each of the states $(1)^1\Delta$ and $(2)^1\Delta$ avoided crossing with the state $(3)^1\Delta$ at $R=2.18\text{\AA}$ while the state $(3)^1\Sigma^+$ avoided crossing with the state $(4)^1\Sigma^+$ at $R=2.3\text{\AA}$. Figure 2 also shows avoided-crossing between states $(2)^1\Pi$ and $(3)^1\Pi$ at $R=2.48\text{\AA}$ and crossing between states $(1)^1\Phi$ and $(3)^1\Pi$ at $R=2.84\text{\AA}$ and $R=3.92\text{\AA}$. Likewise, Figures 3-5 indicate avoided-crossing between electronic states as follows: $(2)^3\Sigma^+$ with $(3)^3\Sigma^+$ at $R=2.36\text{\AA}$, $(1)^3\Delta$ with $(3)^3\Delta$ at $R=2.18\text{\AA}$, $(2)^3\Delta$ with $(4)^3\Delta$ at $R=2.18\text{\AA}$, $(1)^3\Sigma^-$ with $(2)^3\Sigma^-$ at $R=3.2\text{\AA}$, and $(2)^3\Pi$ with $(3)^3\Pi$ at $R=2.48\text{\AA}$ and $R=3.38\text{\AA}$. In Figures 3-5, crossings of electronic states appear in the following manner: $(3)^3\Sigma^+$ with $(1)^3\Delta$ at $R=2.18\text{\AA}$ and $R=2.36\text{\AA}$, $(1)^3\Sigma^-$ with $(4)^3\Delta$ at $R=2.18\text{\AA}$, $(2)^3\Sigma^-$ with $(4)^3\Delta$ at $R=2.72\text{\AA}$, and $(1)^3\Sigma^-$ with $(2)^3\Delta$ at $R=2.18\text{\AA}$ and $R=3.02\text{\AA}$.

3.2 Permanent Dipole Moment Curves

The permanent dipole moment curves (DMCs) have been obtained for the different electronic states of the molecule SrS (Fig. 6-10).

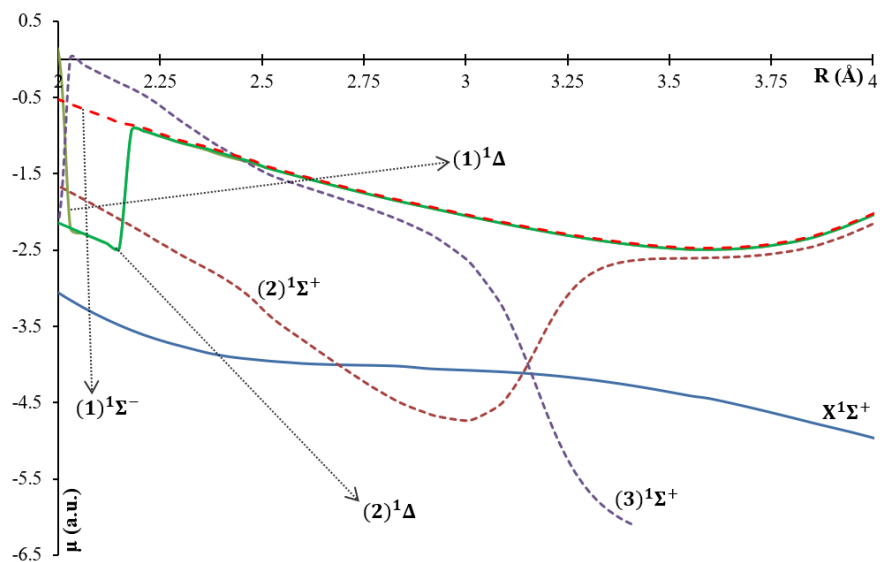


Figure 6. DMCs of the singlet Σ and Δ electronic states of SrS

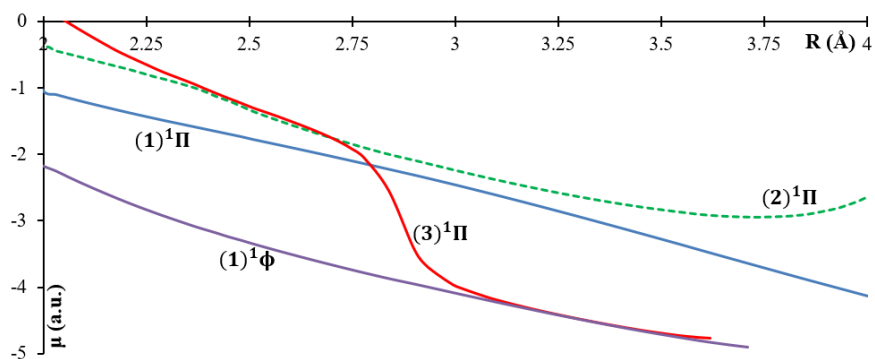
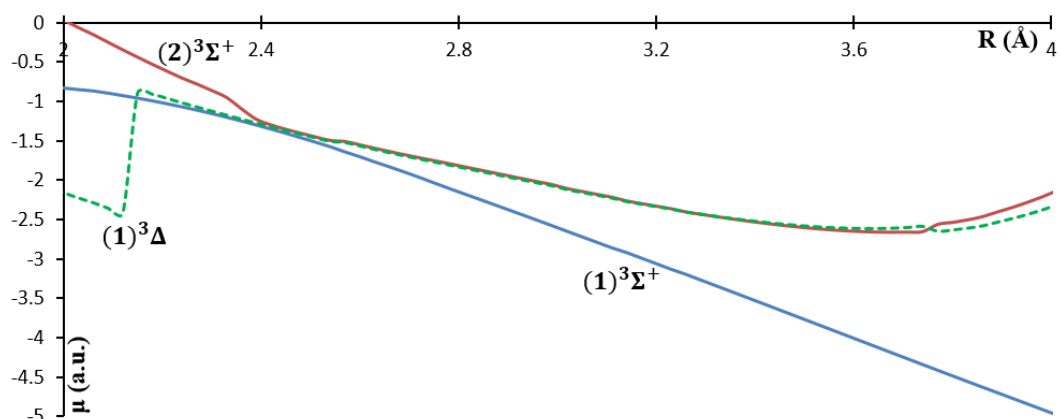
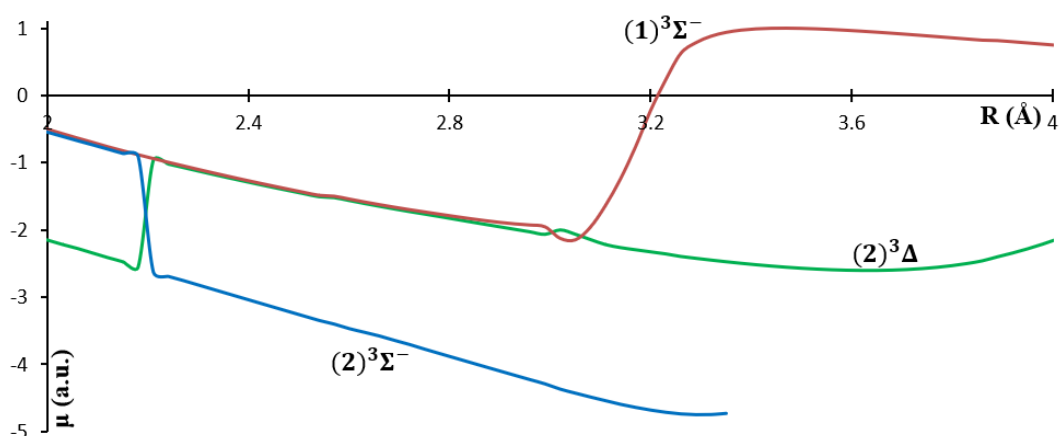
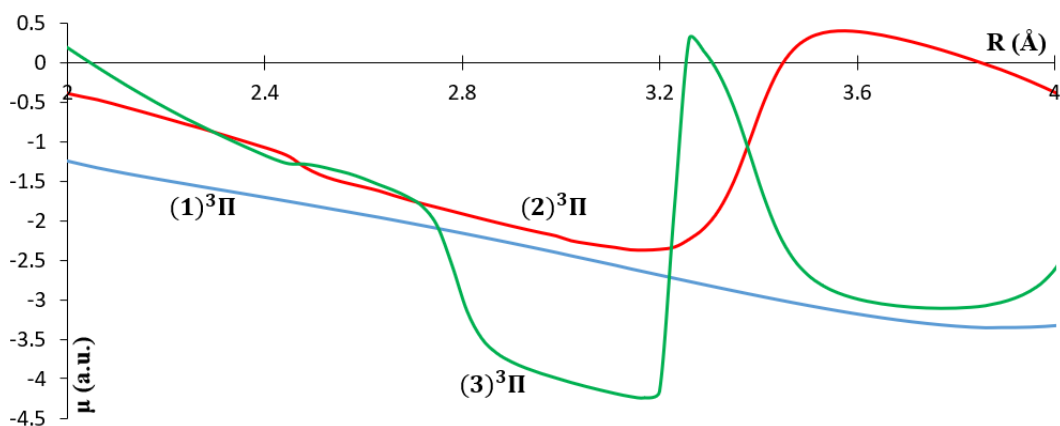


Figure 7. DMCs of the singlet Π and Φ electronic states of SrS

Figure 8. DMCs of some triplet Σ^+ and Δ electronic states of SrSFigure 9. DMCs of some triplet Δ and Σ^- electronic states of SrSFigure 10. DMCs of the triplet Π electronic states of SrS

The permanent dipole moment μ_e is considered as one of the dependable physical properties (Steimle, 2000). It has been computed in this study by fixing the strontium atom (Sr) at the origin and by keeping the sulfur atom (S) free to move along the positive z-axis. Our calculations have been performed with the aid of the MOLPRO program (Werner, Knowles, Knizia, Manby, & Schütz, 2011). Usually, a reverse in the polarity of the atoms is reflected by a sharp change in the directions of the permanent DMCs. This occurs at positions of the internuclear distance (R) where avoided-crossing between electronic states exists in the potential energy curves (PECs). In the present work, one can notice that such sharp changes in the directions of our permanent dipole moment curves match very well with the R locations of avoided-crossing in PECs of SrS. This is an indication of the

good accuracy of the results presented in this study.

4. Conclusion

In the present work, 24 singlet and triplet electronic states of the strontium mono-sulfide molecule have been investigated using the *ab initio* computational method. The CASSCF/MRCI method applied to the SrS molecule, in the $2s+1\Lambda^\pm$ representation, resulted in the calculation of the potential energy curves, the permanent dipole moment (μ_e) curves, the electronic energy with respect to the ground state (T_e), the harmonic frequency (ω_e), the rotational constant (B_e), the internuclear distance (R_e) and the dissociation energy (D_e). The current results generally show good agreement with the results available in literature. To the best of our knowledge, 20 new electronic states of SrS have been examined in this work for the first time. It should be noted that the new study, presented here, may aid in promising experimental investigations on the strontium mono-sulfide molecule in the future.

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