

Electronic Structure and Spectroscopic Studies of the Molecule ScS

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Abstract

Theoretical investigation of the lowest electronic states of ScS molecule, in the representation $2s+1\Lambda^{(+/ -)}$, has been performed via CASSCF and MRCI (single and double excitations without Davidson correction) calculations. The calculated potential energy curves (PECs), permanent dipole moment curves (PDMCs), and spectroscopic constants are reported for the 10 lowest electronic states. The eigenvalues E_v , the rotational constants B_v , and the centrifugal distortion constants D_v have been calculated for various vibrational levels. The comparison of the present results with the available experimental data in literature shows an overall good agreement. To the best of our knowledge, 6 electronic states of the ScS molecule, between 11600 cm^{-1} and 15000 cm^{-1} are not yet observed experimentally and are investigated in the present work for the first time.

Keywords

Ab Initio Calculation, Electronic Structure, Spectroscopic Constants, Potential Energy Curves, Dipole Moments, Vibration-Rotation Calculation

1. Introduction

The molecules containing transition metal are species of chemical and astrophysical importance. Scandium is the first transition metal atom which has only one d-electron in the ground state. Diatomic molecules like ScS are simple transition metal-containing systems in which d-electrons take part in bonding and provide ideal models for understanding the electronic structure and reactivity (chemiluminescent reactions).

To the best of our knowledge, the experimental work for the ScSmolecule is that of Gengler *et al.* [1]-[3]. They studied the $A^2\Pi-X^2\Sigma^+$ and $B^2\Pi-X^2\Sigma^+$ band system of scandium monosulfide, ScS, using Fourier transform emission spectroscopy (FT) and laser excitation spectroscopy (LIF). The only theoretical work for ScS in literature is that of Bauschlicher and Langhoff [4] for the ground $X^2\Sigma^+$ and $(1)^2\Pi$ states using *ab initio* method.

In the present work, *ab initio* investigations of the lowest lying electronic states of the ScS molecule have

been performed via CAS-SCF/MRCI (Complete Active Space Self Consistent Field, Multireference Configuration Interaction) method. Multireference CI calculations (single and double excitations without Davidson corrections) in which the entire CAS-SCF configuration space is used as the reference, are performed to account the correlation effects. The potential energy curves (PECs), the transition dipole moment curves (TDMCs) together with the energy minimum for the ground state T_e , the equilibrium internuclear distance R_e , the harmonic frequency ω_e and the rotational constant B_e have been obtained for the 10 lowest-lying electronic states. Six electronic states have been investigated in the present work for the first time.

2. Method of Calculations

In the present work, *ab initio* investigations of the lowest-lying electronic states of the ScS molecule have been performed via CASSCF method. Multireference CI calculations (single and double excitations without Davidson corrections) were performed to determine the correlation effects. The entire CASSCF configuration space was used as a reference in the MRCI calculation which have been performed via the computational chemistry program MOLPRO [5]. The scandium species is treated in an all electron scheme [6] [7], the 21 electrons of the scandium atom are considered using the contracted Gaussian basis set used by Bauschlicher and Langhoff [4] for s, d, and f functions then we have taken p function from 6 - 31 G** basis set [5] which has 16 diffused functions contracted set of Gaussian functions. The sulfur species is treated as a system with 16 inner electrons taken into account the pseudopotential W^{ps} [8]-[10] together with the corresponding Gaussian basis set. In the range of the internuclear distance R_e around equilibrium distances of its ground state, the ScS molecule is assumed to be mainly ionic as many transition-metals Sc^+S^- . The potential energy calculations for the states $^{2s+1}\Lambda^{(+/-)}$ of the molecule ScS have been carried using a CASSCF method. Among the 37 electrons explicitly considered for ScS (21 electrons for Sc and 16 for S) 27 inner electrons were frozen in subsequent calculations so that 10 valence electrons were explicitly treated. The active space contains 4σ (Sc: 4s, 3d₀), 1π (3d_{±1}) and 1δ (Sc: 3d_{±2}), this corresponds to 6 active molecular orbitals in the C_{2v} symmetry distributed into irreducible representation in the following way: $3a_1$, $1b_1$, $1b_2$, $1a_2$, noted [3111]. The doubly occupied orbitals 2σ (S: 5s, 5p₀), and 1π (S: 5p_{±1}) of sulfur have been considered as inactive in the CASSCF calculations. Correlation effects for the ten valence electrons have been taken into account through multireference calculations MRCI (single and double excitations without Davidson correction) where the entire CASSCF configuration space has been used as reference. Calculations have been performed via the computational program MOLPRO [5] taking advantage of the graphical user interface GABEDIT [11].

3. Results and Discussion

Calculations have been performed for 51 internuclear distances in the range 2.00 Å - 3.02 Å for 10 states in the representation $^{2s+1}\Lambda^{(+/-)}$. The potential energy curves (PECs) for the states $^{2,4}\Sigma$, $^{2,4}\Pi$, $^{2,4}\Delta$ and $^{2,4}\Phi$ in the considered range of Rare drawn respectively in **Figure 1**, **Figure 2**. For each state, transition energies with respect to the minimum energy of the ground state T_e , equilibrium internuclear distance R_e , harmonic frequency ω_e and the rotational constant B_e have been calculated. These constants are displayed in **Table 1** together with the literature values from both theoretical and experimental investigations.

The comparison of our results with the values for T_e calculated by different techniques in the literature for the 10 lowest-lying doublet and quartet electronic states shows that, 7 values are in good agreement where the relative difference is 1.00% [^{c3}Ref.1] $\leq \delta T_e/T_e \leq 4.70\%$ [^{c1-2}Ref.1] for the states $X^2\Sigma^+$, $(2)^2\Sigma^+$ and $(1)^2\Pi$ and one value for the $(1)^2\Pi$ state calculated in Ref. [1] by the SDCI method shows a larger relative difference equal to 13.0%. For ω_e the comparison of our calculated values with the 16 values given in the literature for the 10 lowest electronic states showed an overall good agreement where the relative difference is 0.80% [^{c5}Ref.1 for $(1)^2\Pi$] $\leq \delta\omega_e/\omega_e \leq 12.3\%$ [^{c4}Ref.1 for $(2)^2\Sigma^+$]. Two larger values are obtained for the state $(1)^2\Delta$ calculated in Ref. [1] by the CPF and SDCI + R methods. Since the value of ω_e depends on the shape of the potential energy curves near the minimum, this difference may be explained by the shape of the investigated potential curve by this method. The values of R_e and B_e obtained in literature are in excellent agreement with our calculated values with relative differences 0.3% [^{c2}Ref.1] $\leq \delta R_e/R_e \leq 2.1\%$ [^{c1-1}Ref.1] and 1.6% [^{b3}Ref.4] $\leq \delta B_e/B_e \leq 4.1\%$ [^{b1}Ref.2] respectively for the states $X^2\Sigma^+$, $(2)^2\Sigma^+$ and $(1)^2\Delta$ while the relative differences become larger for the state $(1)^2\Pi$.

By using the canonical functions approach Korek *et al.* [12]-[19] and the cubic spline interpolation between each two consecutive points of the potential energy curves obtained from the *ab initio* calculation of the ScS

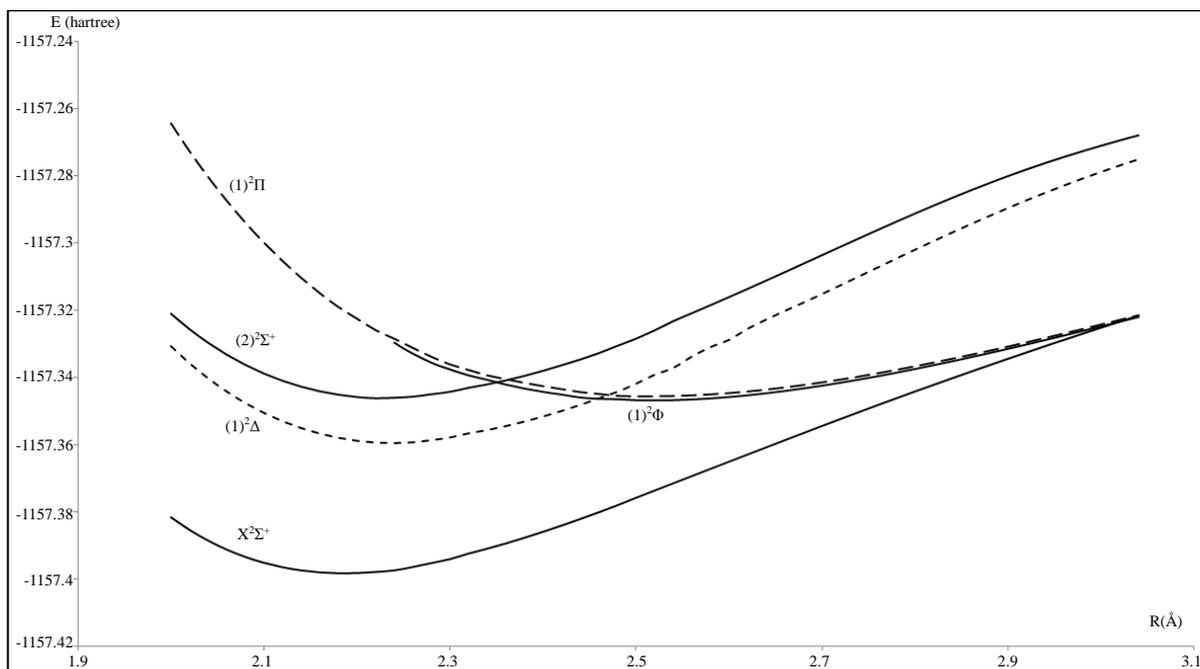


Figure 1. Potential energy curves of the electronic states $X^2\Sigma^+$, $(1)^2\Delta$, $(2)^2\Sigma^+$, $(1)^2\Pi$ and $(1)^2\Phi$ of the molecule ScS.

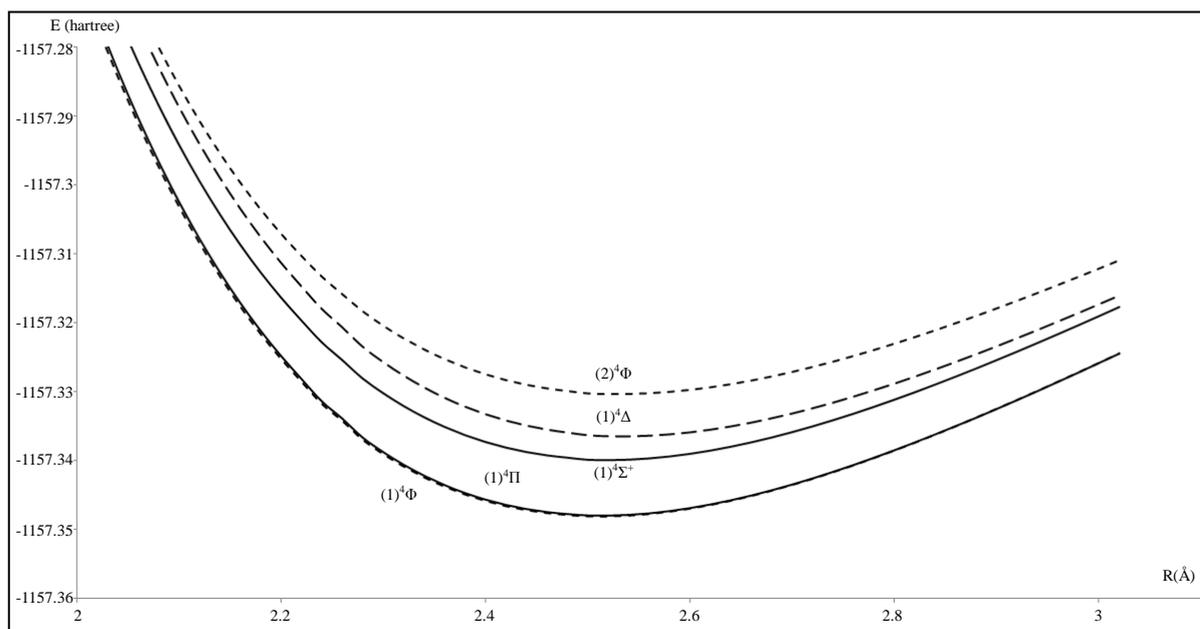


Figure 2. Potential energy curves of the electronic states $(1)^4\Sigma^+$, $(1)^4\Delta$, $(1)^4\Phi$, $(1)^4\Pi$ and $(2)^4\Phi$ of the molecule ScS.

molecule, the eigenvalue E_v , the rotational constant B_v , the centrifugal distortion constants D_v . The abscissas of the turning point R_{\min} and R_{\max} have been calculated for the considered electronic states up to the vibrational levels $v = 10$. These values for the states $(1)^4\Sigma$, $(1)^4\Delta$, $(1)^4\Phi$, $(2)^4\Pi$ and $(2)^4\Phi$ (as illustration) are given in **Table 2**. The absence of the comparison with other results is because of the calculation of these values here for the first time. Then, using the canonical functions approach, the eigenvalues E_v , the rotational constants B_v and the centrifugal distortion constants D_v are calculated for different vibrational levels v for the seven molecular states of ScS ($(1)^2\Pi$, $(2)^2\Sigma$, $(1)^4\Sigma$, $(1)^4\Delta$, $(1)^4\Phi$, $(2)^4\Pi$ and $(2)^4\Phi$). These results are displayed in **Table 2**, respectively. The comparison of our calculated values with those obtained experimentally for the rotational constants B_v and

Table 1. Calculated spectroscopic constants for the lowest 10 electronic states of ScS.

States	T_e (cm ⁻¹)	R_e (Å)	ω_e (cm ⁻¹)	$B_e \times 10^2$ (cm ⁻¹)
	0.0 ^a	2.181 ^a	540.6 ^a	18.929 ^a
	0.0 ^b	2.1375 ^{b-1}		19.7294 ^{b-1}
		2.144 ^{b-2}		19.61 ^{b-2}
		2.139 ^{b-3}		19.71 ^{b-3}
X ² Σ ⁺	0.0 ^c	2.1354 ^{c-1-1}	565.2 ^{c-1}	
		2.167 ^{c-2}	518 ^{c-2}	
		2.177 ^{c-3}	503 ^{c-3}	
		2.126 ^{c-4}	607 ^{c-4}	
		2.125 ^{c-5}	608 ^{c-5}	
		2.229 ^a	581.6 ^a	18.126 ^a
		2.236 ^{c-2}	486 ^{c-2}	
(1) ² Δ	8760 ^a	2.237 ^{c-3}	488 ^{c-3}	
		2.221 ^{c-4}	513 ^{c-4}	
		2.221 ^{c-5}	515 ^{c-5}	
(1) ⁴ Φ	11031	2.513	353.5	14.265
(1) ⁴ Π	11058	2.515	353.1	14.247
(1) ² Φ	11332	2.528	360.0	14.002
	11604 ^a	2.2223 ^a	557.4 ^a	18.240 ^a
(2) ² Σ ⁺	12456 ^{b-1}	2.20391 ^{b-1} 2.2056 ^{b-3}	488.737 ^{b-1}	18.5583 ^{b-1}
	12456 ^{b-3}	2.159 ^{c-3}		18.53 ^{b-3}
		2.143 ^{c-5}	567 ^{c-3}	
			582 ^{c-5}	
	11538.4 ^a	2.497 ^a	494.9 ^a	14.444 ^a
	11090.4 ^{b-1}	2.2079 ^{b-1}		18.4910 ^{b-1}
	11000 ^{c-1-2}			
(1) ² Π	11691 ^{c-2}	2.236 ^{c-2}	468 ^{c-2}	
	11659 ^{c-3}	2.236 ^{c-3}	470 ^{c-3}	
	10698 ^{c-4}	2.218 ^{c-4}	488 ^{c-4}	
	10032 ^{c-5}	2.22 ^{c-5}	491 ^{c-5}	
(1) ⁴ Σ	12828	2.522	350.6	14.158
(1) ⁴ Δ	13581	2.537	344.9	13.995
(2) ⁴ Φ	14928	2.533	333.8	14.043

^aPresent Theoretical study; ^bRef. [1]-[3]; ^(b-1)Ref. [1]; ^(b-2)Ref. [2]; ^(b-3)Ref. [3]; ^cRef. [4].

Table 2. Values of the eigenvalues E_v , the abscissa of the turning points R_{\min} , R_{\max} the rotational constants B_v and the centrifugal distortion constants D_v , for the different vibrational levels of $(1)^2\Pi$, $(2)^2\Sigma^+$, $(1)^4\Sigma^+$, $(1)^4\Delta$, $(1)^4\Phi$, $(2)^4\Pi$, and $(2)\Phi$ electronic states of the ScS molecule.

	v	E_v (cm ⁻¹)	R_{\min} (Å)	R_{\max} (Å)	$B_v \times 10^2$ (cm ⁻¹)	$D_v \times 10^8$ (cm ⁻¹)
$(1)^2\Pi$	0	173.4	1.786	2.593	14.17 ^a 18.45 ^b	9.35 ^a 10.67 ^b
	1	521.2	1.791	2.649	14.15 ^a 18.36 ^b	8.66 ^a 10.83 ^b
	2	872.9	1.795	2.691	14.04	8.73
	3	1224.1	1.799	2.728	14.00	10.63
$(2)^2\Sigma^+$	0	282.9	2.171	2.277	18.16 ^a 18.56 ^b	7.96 ^a 10.82 ^b
	1	826.9	2.133	2.337	18.02 ^a 18.46 ^b	9.45 ^a 10.88 ^b
$(1)^4\Sigma^+$	0	178.1	2.453	2.596	14.13	9.33
	1	525.1	2.405	2.655	14.08	9.52
	2	868.3	2.374	2.698	14.01	9.60
	3	1208.3	2.349	2.734	13.95	9.28
	4	1547.0	2.329	2.767	13.87	9.53
	5	1883.1	2.312	2.797	13.82	9.74
	6	2216.1	2.296	2.825	13.74	8.57
	7	2549.0	2.282	2.852	13.67	
	8	2877.8	2.271	2.877		
	9	3532.0	2.247	2.926		
$(1)^4\Phi$	0	176.9	2.467	2.612	14.24	9.26
	1	529.4	2.417	2.674	14.19	9.50
	2	877.6	2.385	2.718	14.12	9.27
	3	1224.2	2.361	2.796	14.05	9.36
	4	1568.5	2.339	2.789	13.99	9.42
	5	1910.3	2.321	2.821	13.92	9.04
	6	2250.6	2.305	2.849	13.85	9.21
	7	2588.8	2.291	2.878	13.78	8.80
	8	2925.6	2.277	2.904	13.69	
	9	3261.6	2.267	2.931	11.10	
	10	3595.5	2.256	2.955	13.00	

Continued

	0	176.9	2.445	2.588	14.22	9.23
	1	529.3	2.398	2.646	14.17	9.43
	2	877.8	2.367	2.688	14.10	9.28
	3	1224.4	2.343	2.724	14.04	9.25
	4	1569.0	2.323	2.756	13.97	9.45
(2) ⁴ Π	5	1910.70	2.305	2.786	13.90	8.98
	6	2251.10	2.289	2.814	13.83	9.19
	7	2589.4	2.276	2.841	13.76	8.92
	8	2925.8	2.265	2.866	13.68	7.11
	9	3261.4	2.254	2.891		
	10	3594.1	2.241	2.914		
	0	166.1	2.463	2.609	14.01	9.97
	1	497.1	2.414	2.671	13.93	10.36
	2	822.5	2.382	2.715	13.87	10.36
	3	1144.8	2.358	2.753	13.79	9.69
	4	1466.8	2.337	2.786	13.72	10.54
(2) ⁴ Φ	5	1785.4	2.319	2.817	13.66	10.02
	6	2102.1	2.304	2.846	13.58	9.6501
	7	2417.5	2.289	2.874	13.21	
	8	2730.2	2.276	2.901	13.44	
	9	3041.7	2.265	2.925	13.27	
	10	3353.9	2.254	2.951		
	0	171.7	2.445	2.585	13.97	9.25
	1	514.1	2.398	2.642	13.90	9.70
	2	850.4	2.367	2.684	13.85	9.82
	3	1182.6	2.344	2.718	13.78	9.01
	4	1514.9	2.324	2.749	13.71	9.99
(1) ⁴ Δ	5	1843.3	2.307	2.779	13.65	9.44
	6	2169.8	2.291	2.806	13.57	9.05
	7	2495.1	2.278	2.831	13.50	
	8	2817.3	2.267	2.856	13.40	
	9	3138.6	2.256	2.879	13.21	

^aPresent work; ^bRef. [3].

the centrifugal distortion constants D_v showed a good agreement for the state $(2)^2\Sigma$ with averaged relative differences $\delta B_v/B_v = 2.1\%$ and $\delta D_v/D_v = 35.8\%$ for $v = 0$, and these differences are $\delta B_v/B_v = 2.4\%$ and $\delta D_v/D_v = 15.1\%$ for $v = 1$. This agreement becomes less for the state $(1)^2\Pi$, with averaged relative differences $\delta B_v/B_v = 23.2\%$ and $\delta D_v/D_v = 14.1\%$ for $v = 0$, and these differences are $\delta B_v/B_v = 22.9\%$ and $\delta D_v/D_v = 25.1\%$ for $v = 1$.

4. Conclusion

In the present work, the *ab initio* investigation for 10 low-lying electronic states of the ScS molecule has been performed via CASSCF/MRCI method. The potential energy and the dipole moment curves have been determined along with the spectroscopic constants T_e , R_e , ω_e and the rotational constant B_e for these states. The comparison of our results with those obtained theoretically in literature showed a good accuracy. By using the canonical functions approach [12]-[19], the eigenvalue E_v , the rotational constant B_v , the centrifugal distortion constants D_v , and the abscissas of the turning points R_{\min} and R_{\max} were calculated up to the vibrational level $v = 10$. Six electronic states have been investigated in the present work for the first time.

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