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Applying ab initio Calculations to Theoretically Investigate the Electronic Structure of the Calcium Sulfide Molecule CaS

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Abstract

Using the graphical user interface GABEDIT and the computational chemistry software MOLPRO, the *ab initio* calculation method has been applied to explore 25 low-lying singlet and triplet electronic states, including the $X^1\Sigma^+$ ground state, of the calcium sulfide molecule CaS in the $^{2s+1}\Lambda^{\pm}$ representation. The multi-reference configuration interaction with Davidson correction (MRCI+Q) and the complete active space self-consistent field (CASSCF) calculations were performed to obtain the potential energy curves in terms of the internuclear distance R. The permanent dipole moments μ_e of these low-lying electronic states of CaS have been investigated, in addition to the corresponding spectroscopic constants (including the electronic energy with respect to the ground state T_e, the equilibrium internuclear distance R_e, the harmonic vibrational frequency ω_e, the rotational constant B_e, and the equilibrium dissociation energy D_e). In the present work, 19 new singlet and triplet CaS electronic states were investigated for the first time. In addition, it is noticeable that the current results and those already available in literature are in good agreement.

Keywords: calcium sulfide, electronic structure, potential energy curves, permanent dipole moment curves, spectroscopic constants, *ab initio* calculation, computational chemistry

1. Introduction

The properties of metal sulfides have been of great interest among scientists in the domain of chemistry and other related fields due to their wide range of applications that are based on their unique metal-sulfur bond nature (Halfen, Apponi, Thompsen, & Ziurys, 2001). For instance, in reactions involving proteins in biochemistry, metal sulfides play the role of sulfur-donating ligands (Holm, Kennepohl & Solomon, 1996) (Halfen, Apponi, Thompsen, & Ziurys, 2001) (Janczyk & Ziurys, 2006). These compounds are also important in high temperature chemistry, chemical vapor deposition and corrosion processes (Bradley, 1989) (Halfen, Apponi, Thompsen, & Ziurys, 2001). Besides, some applications in astrophysics are related to alkaline-earth metal sulfides in specific (Takano, Yamamoto, & Saito, 1989) (Janczyk & Ziurys, 2006).

Not many studies have been performed on the calcium sulfide molecule and they have been restricted to very few low-lying electronic states even though several theoretical and experimental investigations were done on various other alkaline-earth metal sulfides (Huber & Herzberg, 1979) (Hüttner, 2012). Experimentally, Blues and Barrow were the first to study the absorption of CaS at around 1900˚C in the year 1968, where only 2 states were obtained and the ground state was specified as $X^1\Sigma^+$ (Blues & Barrow, 1969). In 1987, a theoretical study (based on *ab initio* calculations) was conducted, by Partridge *et al.,* on alkaline-earth mono-sulfides, including calcium mono-sulfide, in which 5 computational methods were used on the molecule CaS and 3 of its electronic states were reported (Partridge, Langhoff, & Bauschlicher, 1988). More experimental studies were done on CaS between the years 1989 and 2002. Takano *et al.* used a source-modulated microwave spectrometer to observe rotational transitions of this molecule (in the $X^1\Sigma^+$ electronic state) in the frequency region 200 to 300 GHz (Takano, Yamamoto, & Saito, 1989). Jarman *et al.* obtained 3 electronic states (2 singlet and 1 triplet Π states) in the blue region of calcium sulfide's spectrum (Jarman, Hailey, & Bernath, 1992). Andersson and Davis studied the singlet $X^1\Sigma^+$ and $(2)^1\Sigma^+$ states of CaS by a Fourier Transform Spectrophotometer and calculated the corresponding principal molecular constants (Andersson & Davis, 2001). The same 2 states were also inspected again using high-resolution laser excitation spectroscopy by Melville & Coxon (Melville & Coxon, 2002).

In the current study, the *ab initio* method was used to investigate several low-lying electronic states of calcium

sulfide, in the $^{2s+1}\Lambda^{\pm}$ representation, by means of the complete active space self-consistent field (CASSCF) and the multi-reference configuration interaction (MRCI) with Davidson correction (+Q) computational approaches. In this work, we present 25 electronic states of CaS, out of which 19 new low-lying states are examined for the first time. Their corresponding PECs (potential energy curves) and PDMCs (permanent dipole moment curves) are demonstrated. Moreover, we were able to calculate, for 18 electronic states, the spectroscopic constants T_e (the electronic energy with respect to the ground state), R_e (the equilibrium internuclear distance), ω_e (the harmonic vibrational frequency), B_e (the rotational constant) and D_e (the equilibrium dissociation energy).

2. Computational Approach

The computational chemistry software MOLPRO (Werner, Knowles, Knizia, Manby, & Schütz, 2011) has been used, in the present work, with the aid of the graphical user interface GABEDIT (Allouche, 2010) to perform *ab initio* calculations to the diatomic molecule calcium sulfide. The state averaged CASSCF (complete active space self-consistent field) and the MRDSCI+Q (multi-reference doubly and singly configuration interaction with Davidson correction) methods have been applied to study the low-lying singlet and triplet electronic states of the CaS compound. The neutral calcium atom Ca with 20 electrons (10 core and 10 valence electrons), has been treated, for *s*, *p* and *d* functions (*6s, 6p, 5d*)/[*4s, 4p, 2d*], with the Wood-Boring (WB) energy-consistent effective core potential ECP10MWB basis set described by Kaupp *et al.* (Kaupp, Schleyer, Stoll & Preuss, 1991) that represents a quasi-relativistic theoretical level of reference. As for the sulfur atom S of 16 electrons (16 valence electrons), in its neutral state, it has been treated with the correlation consistent polarized valence quintuple-zeta cc-pV5Z basis set given by Woon and Dunning (Woon & Dunning, 1993) for the *s* and *p* functions (*20s, 12p, 4d, 3f, 2g, 1h*)/[*7s, 6p, 4d, 3f, 2g, 1h*]. 10 electrons (the 10 electrons of Ca), out of the 36 electrons of calcium sulfide, are kept in the core of the molecule while the other 26 valence electrons (10 electrons from Ca and 16 electrons from S) are considered outside its core. The wave functions of these 26 valence electrons are defined by 24 active molecular orbitals that are formed on *3s, 3p, 3d, 4s, 4p* and *5s* of Ca and *1s*, *2s, 2p, 3s, 3p and 4s* of S. During calculation, 20 electrons are frozen, by keeping them doubly occupied, in the *3s* and *3p* orbitals of calcium and the *1s*, *2s, 2p,* and *3s* orbitals of sulfur. Therefore, only the other 6 valence electrons are explicitly treated later. The active space orbitals, in the C_{2v} point group symmetry, are distributed into the irreducible representations a_1, b_1, b_2 and a_2 as $6a_1$, $2b_1$, $2b_2$ and $0a_2$, denoted by [6, 2, 2, 0]. These molecular orbitals, contained in the active space, are at least 6σ (Ca: $3d_0$, *4s*, $4p_0$, *5s*; S: $3p_0$, *4s*), 3π (Ca: $3d_{\pm1}$, $4p_{\pm1}$; S: $3p_{\pm1}$) and 1δ (Ca: $3d_{\pm2}$).

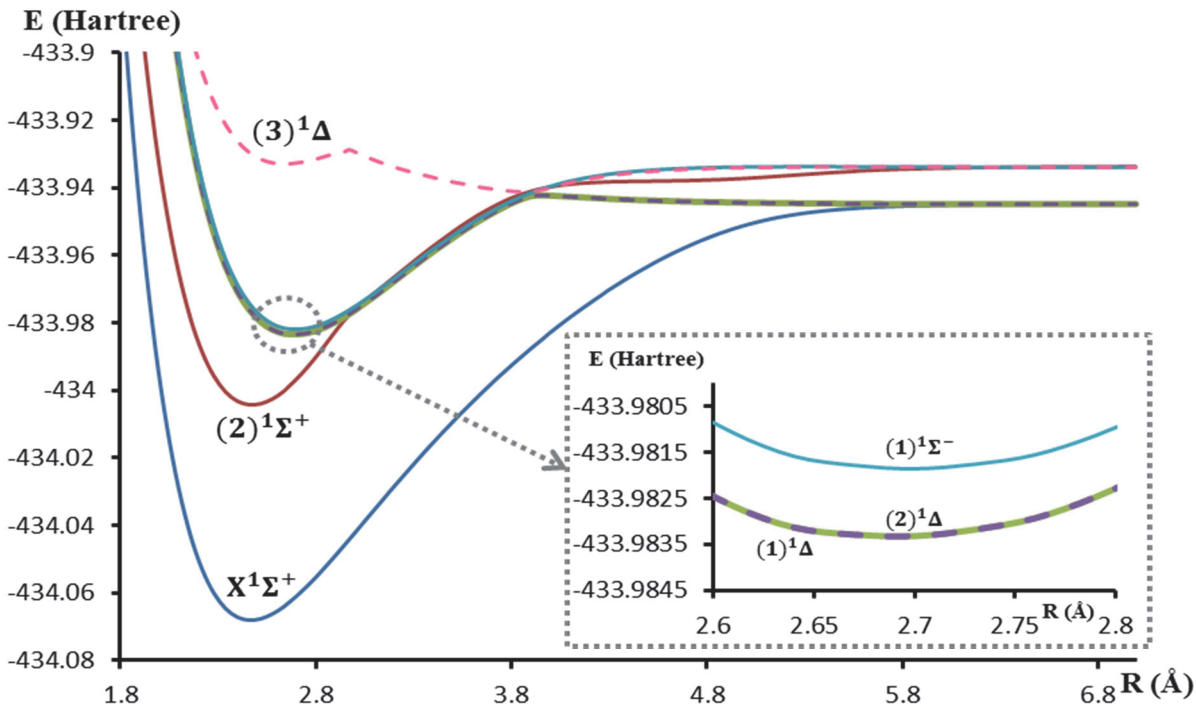

Figure 1. PECs of the singlet Σ and Δ electronic states of CaS

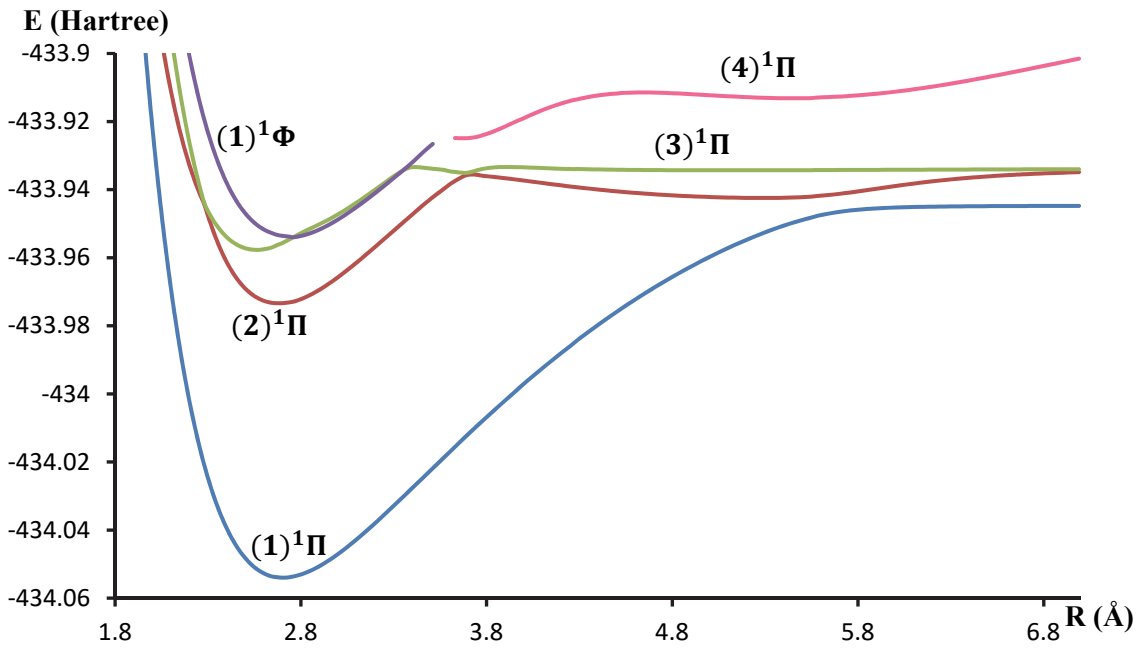

Figure 2. PECs of the singlet Π and Φ electronic states of CaS

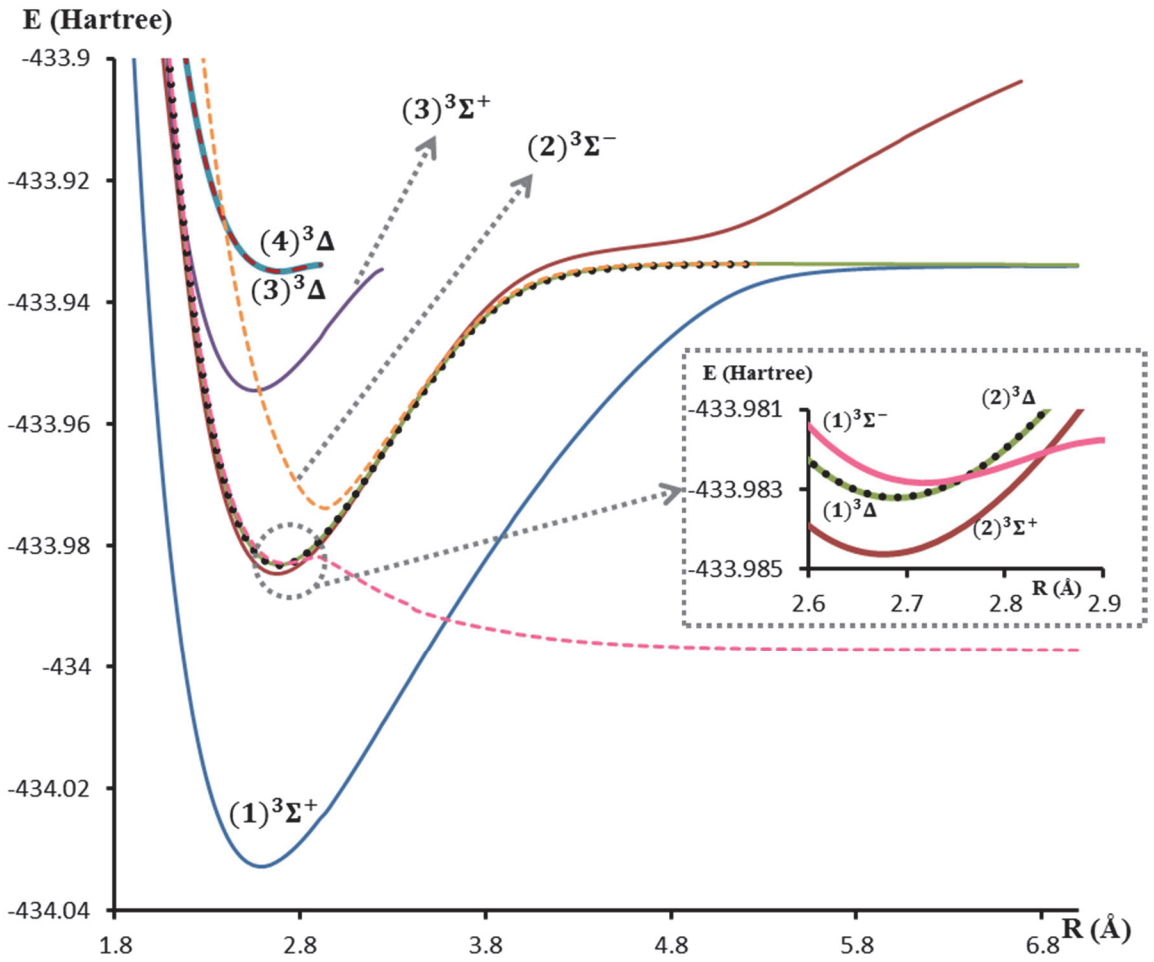

Figure 3. PECs of the triplet Σ and Δ electronic states of CaS

3. Results and Discussion

3.1 Potential Energy Curves

As a function of the internuclear distance R, the potential energy curves (PECs) have been computed and demonstrated for 25 low-lying singlet and triplet molecular electronic states of calcium sulfide, in the $^{2s+1}\Lambda^{\pm}$ representation (Figs. 1-4). This PEC calculation has been applied, in the range 1.8 Å ≤ R ≤ 6.99 Å, to 174 internuclear distances.

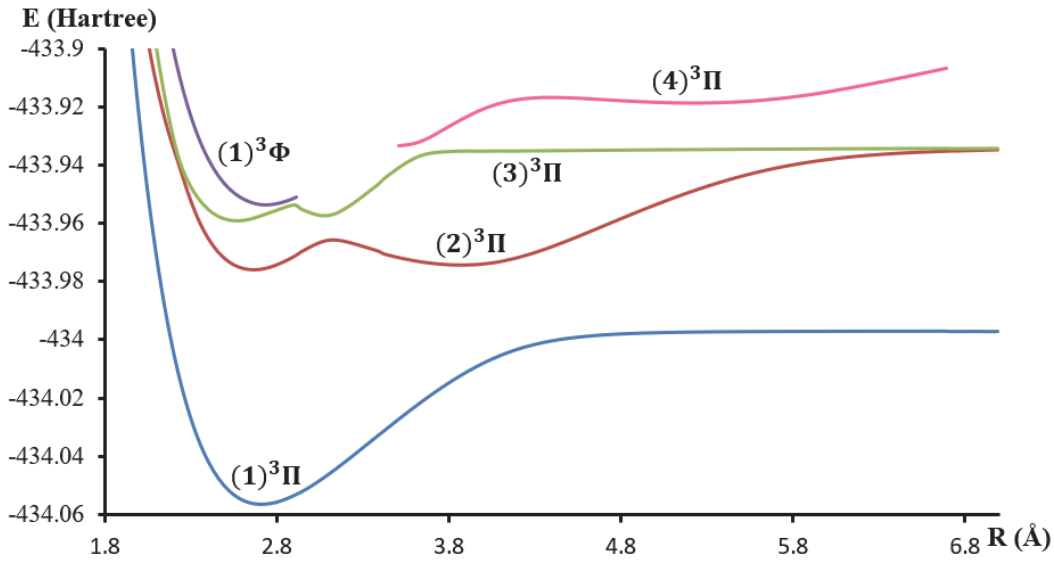

Figure 4. PECs of the triplet Π and Φ electronic states of CaS

In Figures 1-4, various locations of crossing and avoided-crossing, in the PECs, can be spotted between the electronic states of CaS. Sites of crossing between the PECs of the electronic states are noticed to occur as follows: $(2)^1\Sigma^+$ with $(1)^1\Delta$ at R=3Å, $(1)^1\Sigma^-$ with $(3)^1\Delta$ at R=3.93Å, $(3)^1\Pi$ with $(1)^1\Phi$ at R=2.76Å and R=3.36Å, $(3)^3\Sigma^+$ with $(1)^3\Delta$ at R=2.16Å, $(2)^3\Sigma^+$ with $(1)^3\Delta$ at R=3.33Å, $(1)^3\Sigma^-$ with $(2)^3\Delta$ at R=2.76Å and $(2)^3\Sigma^-$ with $(4)^3\Delta$ at R=2.4Å. As for the sites of avoided-crossing between the PECs of the electronic states, they appear in the following cases: $X^1\Sigma^+$ with $(2)^1\Sigma^+$ at R=5.1Å, $(2)^1\Pi$ with $(3)^1\Pi$ at R=2.28Å and R=3.72Å, $(3)^1\Pi$ with $(4)^1\Pi$ at R=3.75Å, $(1)^1\Pi$ with $(2)^1\Pi$ at R=5.67Å, $(1)^1\Pi$ with $(4)^1\Pi$ at R=5.31Å, $(2)^1\Delta$ with $(3)^1\Delta$ at R=3.9Å, $(1)^3\Sigma^+$ with $(2)^3\Sigma^+$ at R=5.07Å, $(2)^3\Sigma^+$ with $(3)^3\Sigma^+$ at R=2.16Å, $(1)^3\Sigma^-$ with $(2)^3\Sigma^-$ at R=2.91Å, $(2)^3\Pi$ with $(3)^3\Pi$ at R=2.22Å and R=3.09Å, $(3)^3\Pi$ with $(4)^3\Pi$ at R=3.69Å, $(1)^3\Pi$ with $(2)^3\Pi$ at R=4.11Å and $(2)^3\Pi$ with $(4)^3\Pi$ at R=5.43Å.

3.2 Spectroscopic Constants

Spectroscopic constants of the CaS molecule have been calculated for 18 singlet and triplet electronic states by fitting, into a polynomial in R, the potential energy values around the equilibrium internuclear distance. These constants include the electronic energy with respect to the ground state, the equilibrium internuclear distance, the harmonic vibrational frequency, the rotational constant and the equilibrium dissociation energy, denoted as T_e, R_e, ω_e, B_e and D_e respectively (Table 1). For some electronic states, where the minima of their PECs occur at regions of crossing or avoided-crossing between states, the spectroscopic constants have not been calculated.

The results, presented in Table 1, have been compared to those available in previous theoretical and experimental studies (Blues & Barrow, 1969) (Marcano & Barrow, 1970) (Partridge, Langhoff, & Bauschlicher, 1988) (Takano, Yamamoto, & Saito, 1989) (Jarman, Hailey, & Bernath, 1992) (Andersson & Davis, 2001) (Melville & Coxon, 2002). The molecular spectroscopic constants of CaS, computed here, show good agreement with the investigations found in earlier literature, especially when linked to prior experimental outcomes. The only remarkable difference in the T_e values can be noticed with respect to the CASSCF theoretical results of Partridge *et al.*; this is associated with the challenging nature (regarding the process of selecting configurations) of the CASSCF method which may be viewed as a full configuration interaction calculation in a restricted configuration space. On the other hand, the MRCI method (used here) is more likely to result in better enhanced computations (Kohanoff, 2006).

Table 1. Spectroscopic constants computed for the singlet and triplet electronic states of the CaS molecule.

State	T_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})	10^8D_e (cm^{-1})
$X^1\Sigma^+$	0[a]	2.469[a]	381.0747[a]	0.155153[a]	10.27[a]
	0[b]	2.3178[b]	462.23[b]	0.17667[b]	10.2[b]
	0[c]	2.342[c]	455[c]		
	0[d,1]	2.374[d,1]	435[d,1]		
	0[d,2]	2.379[d,2]	441[d,2]		
	0[d,3]	2.343[d,3]	442[d,3]		
	0[e]	2.317751[e]	462.3[e]	0.1766756[e]	10.32014[e]
	0[f]		462.22856[f]	0.176675662[f]	10.31796[f]
	0[g,1]		462.263[g,1]	0.176673[g,1]	10.329[g,1]
	0[g,2]		462.265[g,2]	0.176672[g,2]	10.324[g,2]
	0[h]	2.31770[h]	462.273[h]	0.176683[h]	
$(1)^3\Pi$	2516.81[a]	2.709[a]	296.8640[a]	0.128871[a]	9.71[a]
	8658[d,1]	2.637[d,1]	326[d,1]		
	4415[d,2]	2.641[d,2]	323[d,2]		
	5389[d,3]	2.600[d,3]	338[d,3]		
	5554[d,4]	2.642[d,4]	321[d,4]		
	6528[d,5]	2.597[d,5]	327[d,5]		
$(1)^1\Pi$	3072.38[a]	2.701[a]	303.0692[a]	0.129663[a]	9.47[a]
	6901[d,1]	2.600[d,1]	337[d,1]		
$(1)^3\Sigma^+$	7707.90[a]	2.591[a]	317.5300[a]	0.140937[a]	11.10[a]
$(2)^1\Sigma^+$	13945.30[a]	2.477[a]	382.8908[a]	0.154199[a]	10.01[a]
	15194.44[b]	2.3864[b]	409.04[b]	0.16666[b]	10.8[b]
	15220.775[g,1]		409.062[g,1]	0.166680[g,1]	11.10[g,1]
	15220.775[g,2]		409.064[g,2]	0.1666769[g,2]	11.08[g,2]
	15194.4281[h]	2.38626[h]	409.077[h]	0.166676[h]	
$(2)^3\Sigma^+$	18299.54[a]	2.675[a]	308.1912[a]	0.132223[a]	9.71[a]
$(1)^1\Delta$	18574.87[a]	2.687[a]	305.8835[a]	0.131230[a]	9.03[a]
$(2)^1\Delta$	18576.21[a]	2.687[a]	300.6138[a]	0.131255[a]	9.35[a]
$(1)^3\Delta$	18609.96[a]	2.688[a]	299.8309[a]	0.130914[a]	9.98[a]
$(1)^1\Sigma^-$	18900.54[a]	2.694[a]	299.4578[a]	0.130704[a]	8.94[a]
$(2)^3\Pi$	20195.36[a]	2.664[a]	305.9822[a]	0.133271[a]	10.11[a]
$(2)^1\Pi$	20761.92[a]	2.685[a]	280.4175[a]	0.131217[a]	11.66[a]
$(3)^3\Pi$	23915.30[a]	2.565[a]	334.6192[a]	0.143807[a]	10.62[a]
	23177.7302[f]		334.0689[f]	0.1459763[f]	23.64[f]
$(3)^1\Pi$	24212.37[a]	2.558[a]	330.3429[a]	0.145328[a]	8.84[a]
	23231.7208[f]		335.7861[f]	0.14745846[f]	12.793[f]
$(3)^3\Sigma^+$	24883.38[a]	2.555[a]	303.8587[a]	0.144910[a]	13.16[a]
$(1)^3\Phi$	25112.39[a]	2.732[a]	315.9403[a]	0.126791[a]	8.05[a]
$(3)^3\Delta$	29176.50[a]	2.690[a]	247.4218[a]	0.130619[a]	15.45[a]
$(3)^1\Delta$	29648.01[a]	2.625[a]	319.5126[a]	0.137125[a]	11.03[a]

[a] Present work.

[b] Experimental work by Blues and Barrow (Blues & Barrow, 1969).

[c] Theoretical estimation by Marcano and Barrow (Marcano & Barrow, 1970).

[d] Theoretical work by Partridge *et al.* using 5 methods (d1: CASSCF, d2: CCI, d3: CCI (*3s3p*), d4: MRCI, d5: MRCI+Core) (Partridge, Langhoff, & Bauschlicher, 1988).

[e] Experimental work by Takano *et al.* (Takano, Yamamoto, & Saito, 1989).

[f] Experimental work by Jarman *et al.* (Jarman, Hailey, & Bernath, 1992).

[g] Experimental work by Andersson and Davis (g1: Direct Approach, g2: Term Value Method) (Andersson & Davis, 2001).

[h] Experimental work by Melville and Coxon (Melville & Coxon, 2002).

3.3 Permanent Dipole Moment Curves

Considering the fact that it is one of the reliable physical properties (Steimle, 2000), the permanent dipole moment μ_e has been calculated using the computational chemistry program MOLPRO (Werner, Knowles, Knizia, Manby, & Schütz, 2011). The calculation is done by keeping, along the positive z-axis, the sulfur atom S free to move while fixing the calcium atom Ca at the origin. Accordingly, the permanent dipole moment curves (PDMCs) have been presented, in this study, for several molecular electronic states of the CaS molecule (Figs. 5-8).

Generally, a sharp change in the directions of the PDMCs reveals a reverse in the polarity of the atoms. Such phenomena appear at locations of the internuclear distance (R) where, in the potential energy curves (PECs), electronic states avoid crossing. In the current calcium sulfide investigation, the R sites of avoided-crossing in our PECs are actually well reflected in the sharp variations in the directions of our PDMCs (note that at R values of avoided-crossing in PECs, the PDMCs of the corresponding states may intersect due to the sharp changes in the directions of the PDMCs). Consequently, it can be deduced that the present permanent dipole moment results are of good precision.

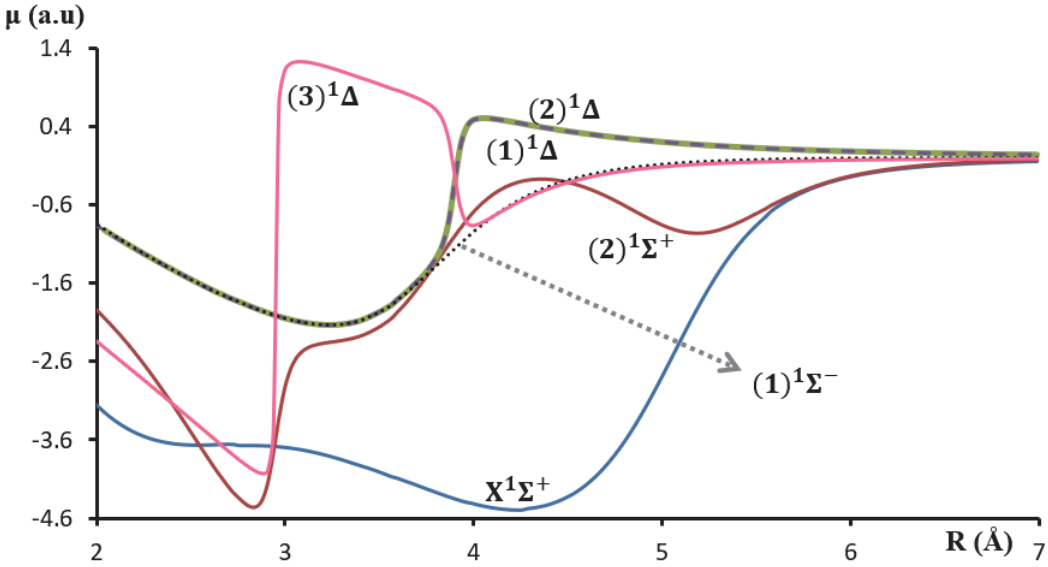

Figure 5. PDMCs of the singlet Σ and Δ electronic states of CaS

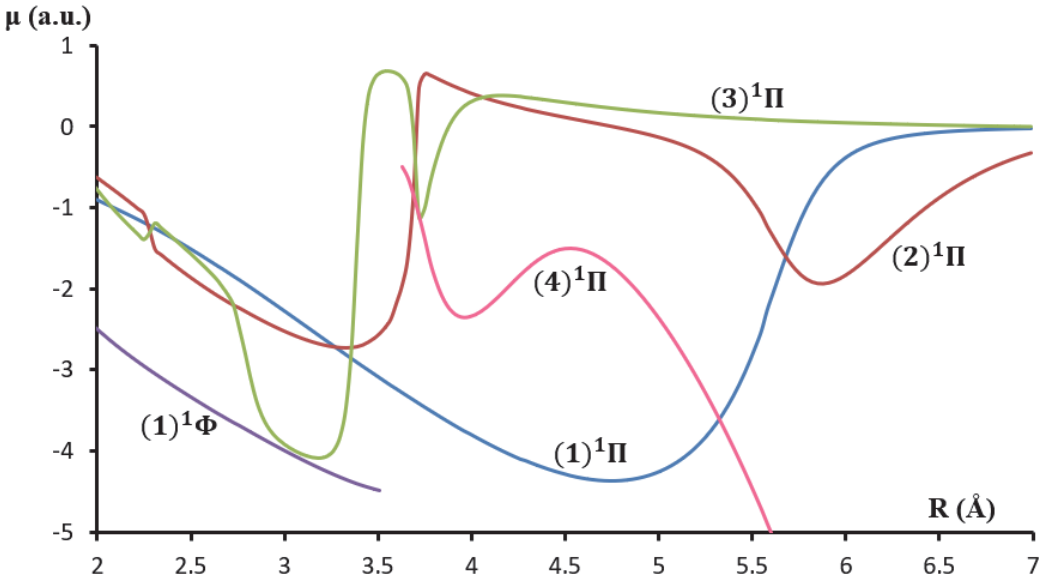

Figure 6. PDMCs of the singlet Π and Φ electronic states of CaS

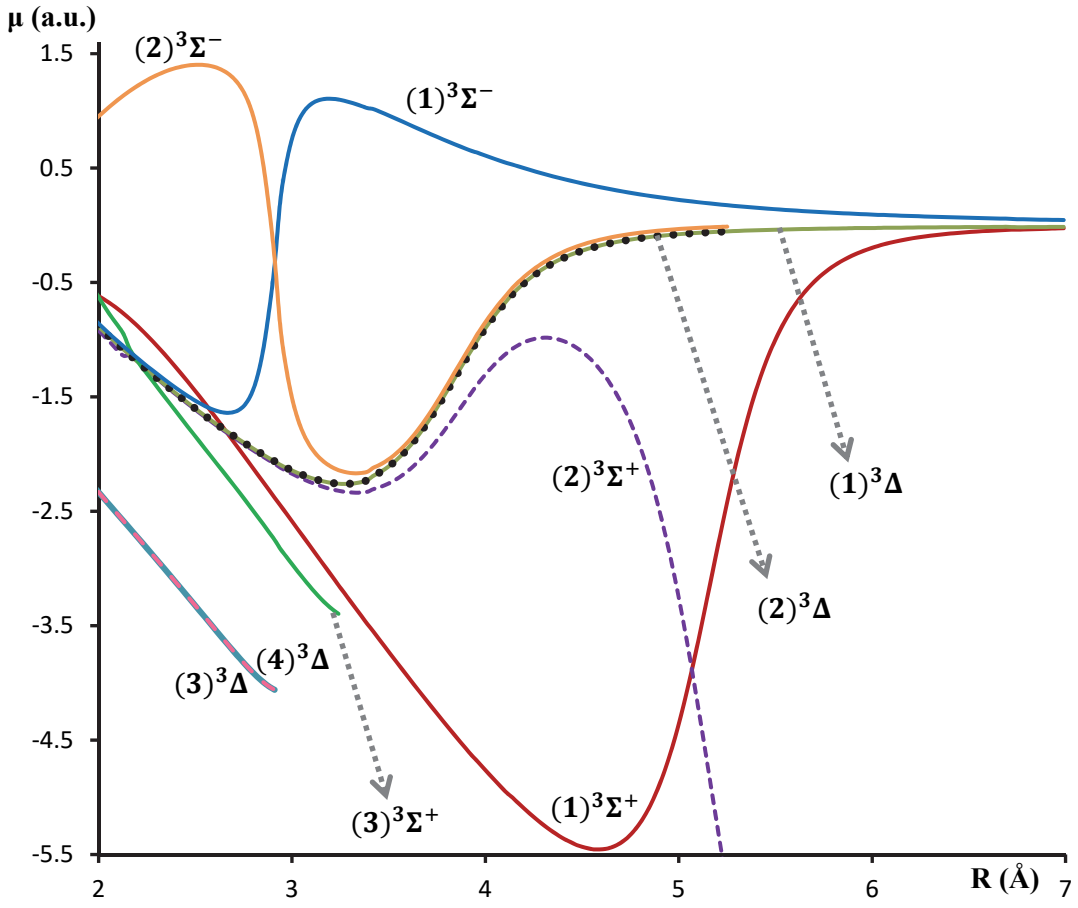

Figure 7. PDMCs of the triplet Σ and Δ electronic states of CaS

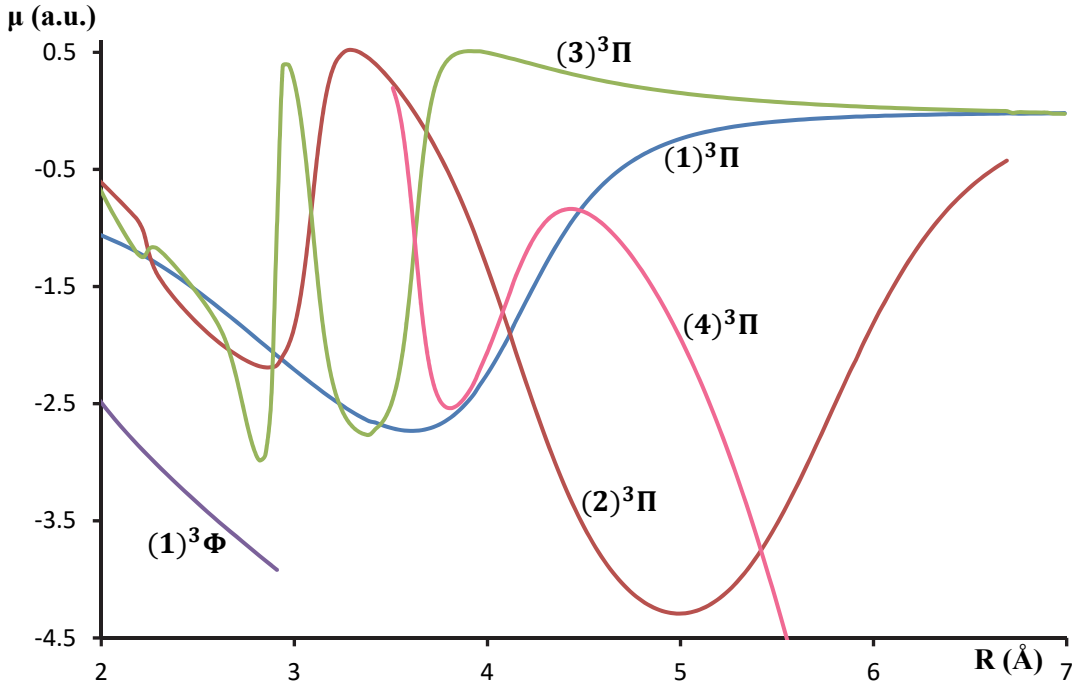

Figure 8. PDMCs of the triplet Π and Φ electronic states of CaS

4. Conclusion

In the current study, 25 molecular electronic states of the calcium sulfide, of which 11 are singlet and 14 are triplet, have been examined via the *ab initio* calculation method. The CASSCF and MRCI computational methods have been applied to the calcium mono-sulfide molecule CaS, in the $^{2s+1}\Lambda^{\pm}$ representation. Thus, the potential energy curves and the permanent dipole moment curves of this molecule have been presented. The spectroscopic constants (T_e: the electronic energy with respect to the ground state, R_e: the internuclear distance at equilibrium, ω_e: the harmonic vibrational frequency, B_e: the rotational constant and D_e: the dissociation energy) have also been computed. The results of the present work are in relatively good agreement with the results of previous available literature. 19 new electronic states of CaS have been, to the best of our knowledge, investigated here for the first time. Hopefully, we believe our new study may provide sufficient and promising assistance in any future experimental examination applied to the calcium sulfide molecule.

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