Electronic Structure and Dipole Moment Calculations of the Electronic States of the Molecule ZnS

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Abstract

In this study, the low lying electronic states and spectroscopy of diatomic molecule ZnS in addition to its dipole moments have been investigated by performing highly correlated ab initio calculations, the Complete Active Space Self Consistent Field (CASSCF) method with Multi Reference Configuration Interaction (MRCI+Q) for an accurate picture for these states. The proposed study includes information about the potential energy curves of the lowest 12 singlet and 9 triplet electronic states of the molecule ZnS, in the representation $^{2s+1}\Lambda^{(+/-)}$. Nine of these states have been studied here for the first time. The harmonic frequency w_e, the internuclear distance r_e, the electronic energy with respect to the ground state T_e, the rotational constant B_e, and the permanent dipole moment μ have been calculated, compared and compiled with the available existing data to illustrate the electronic characteristics. The comparison of these values reveals a very good agreement.

Keywords: *ab initio* calculation, electronic structure, spectroscopic constants, potential energy curves, dipole moments

1. Introduction

The zinc Chalcogenides (ZnS, ZnSe, and ZnTe) are diatomic molecules yield from the combination between a metal of group IIb (Zn, Cd, Hg) with a valence electronic configuration ns^2 and a chalcogen (O, S, Se, Te) with a valence electronic configuration $n's^2n'p^4$ (Chamboud 2008). These compounds have the wide band gap, the high iconicity (0.77, 0.63, and 0.49 respectively) of chemical bond, the smaller energy of formation of vacancies, and they are very sensitive to any strain (Peterson, Spheler, Singleton, 2007).

These compounds are the promising materials for their use in many optoelectronic applications. The zinc sulphide ZnS exists both in natural and synthetic crystalline form possessing cubic or hexagonal structures. The poly-nuclear diatomic molecule ZnS is used in luminescent materials such as X-ray screens to glow in the dark products. With copper this molecule is used in electroluminescent panels and also exhibit phosphorescence. ZnS is used also for infrared optical materials such as optical window or shaped into lenses, pigment which with barium sulfate forms lithopone used for interior paints and a pigment used to change color of reflected or transmitted ray. Also it is commonly used as a source of evaporation and as a semiconductor for electronic and solar applications. Away from lab, ZnS is usually produced from waste materials such as cosmetic, pharmaceutical, and rubber industries. Thus, they perform a toxicity and harmful impact on aquatic life as disturbing the dissolved oxygen content of the water (Wikipedia).

The aim of this study is to calculate the near-equilibrium potential energy of the lowest electronic states of diatomic molecule zinc sulfide ZnS. $^1S^+$ and ^3P are the ground and the first exited states respectively. The $^1S^+$ $(1s^2,1d^4,1p^4,2s^2,3s^2,2p^4,4s^0)$ is known always as shorter equilibrium band energy dissociation and larger dipole moment compared to those of ^3P $(1s^2,1d^4,1p4,2s^2,3s^2,2p^3,4s^1)$ where state $^1S^+$ is stabilized relative to ^3P. Because of these properties, any small change in the bond length leads to a great change in the electronic structure without involving a large quantity of energy (Chamboud 2008).

2. Method

The given study is based on configuration interaction (CI) and on Multi-Reference configuration interaction methods (MRCI) where the CI calculation includes instantaneous electron correlation. It is also called as configuration mixing method (CM) where it involves first-higher order corrections to the Hartree-Fock wave

function. It is useful for calculating excited states of molecules, where the Hartree-Fock fails (Atkins & Friedman).

In the present work, the low-lying singlet, and triplet electronic states of the molecule ZnS are calculated using Complete Active Space Self Consistent Field (CASSCF) procedure followed by a multireference configuration interaction (MRCI+Q with Davidson correction) treatment for the electron correlation. The entire CASSCF configuration space was done by the means of the computational chemistry program MOLPRO (MOLPRO) taking advantage of the graphical user interface GABEDIT (Allouche 2011).

The 30 electrons of zinc atom and the 16 electrons of sulfur atom are taken as a system relative to ECP10MDF as basis set for s, p, and d orbitals, and ECP10MWB basis z-set for s and p orbitals with d orbital which is treated by aug-cc-PVDZ basis set respectively. Therefore, the diatomic molecule is studied as 26 free electrons among 12 electrons were frozen and 14 as valance electrons corresponding to active orbitals were explicitly treated with 10 valance orbitals.

3. Results

3.1 Potential Energy Curves and Spectroscopic Constants

The potential energy curves (PECs) for the 21 singlet, and triplet electronic states, in the representation $^{2s+1}\Lambda^{(+/-)}$, of the molecule ZnS were performed using the MRCI+Q for internuclear distances calculations in the range $1.4\text{Å} \leq R_e \leq 4.4\text{Å}$ (figs. (1-2)) and in the range $1.5\text{Å} \leq R_e \leq 9.6\text{Å}$ (figs.(3-4))
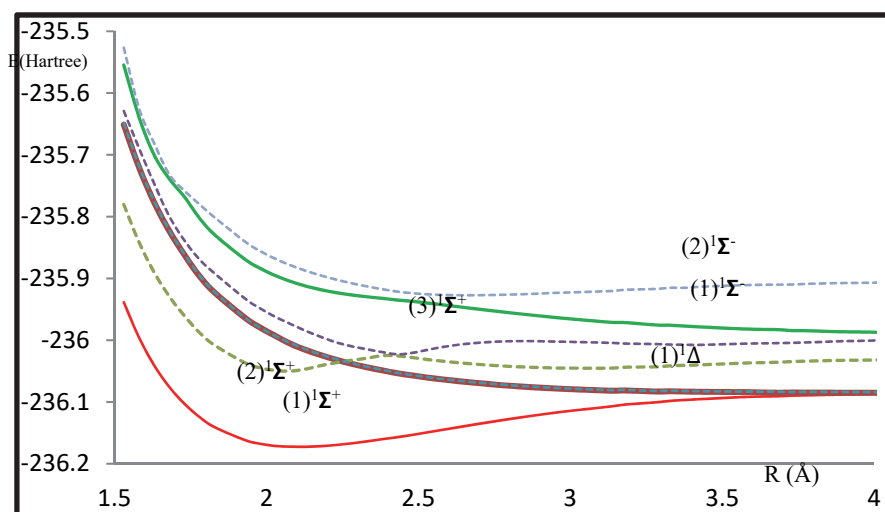

Figure 1. Potential Energy Curves of the $^1\Sigma^{\pm}$ and $^1\Delta$ States of the Molecule ZnS
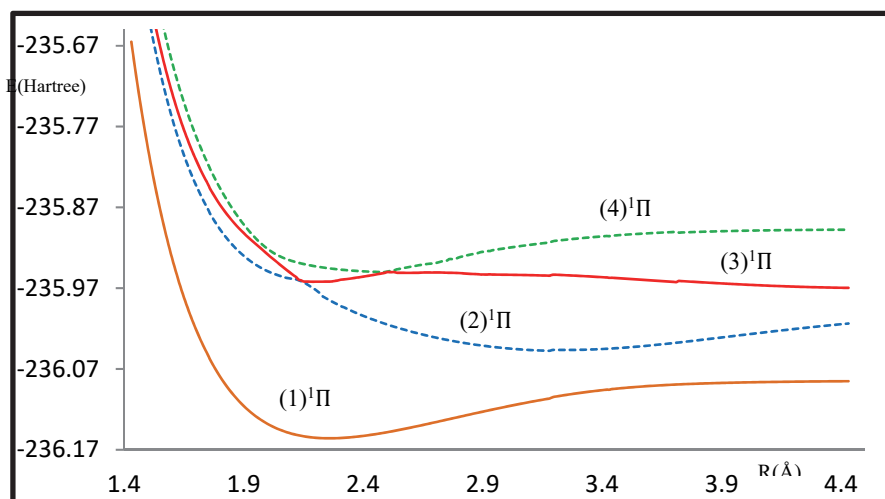

Figure 2. Potential Energy Curves of the $^1\Pi$ States of the Molecule ZnS
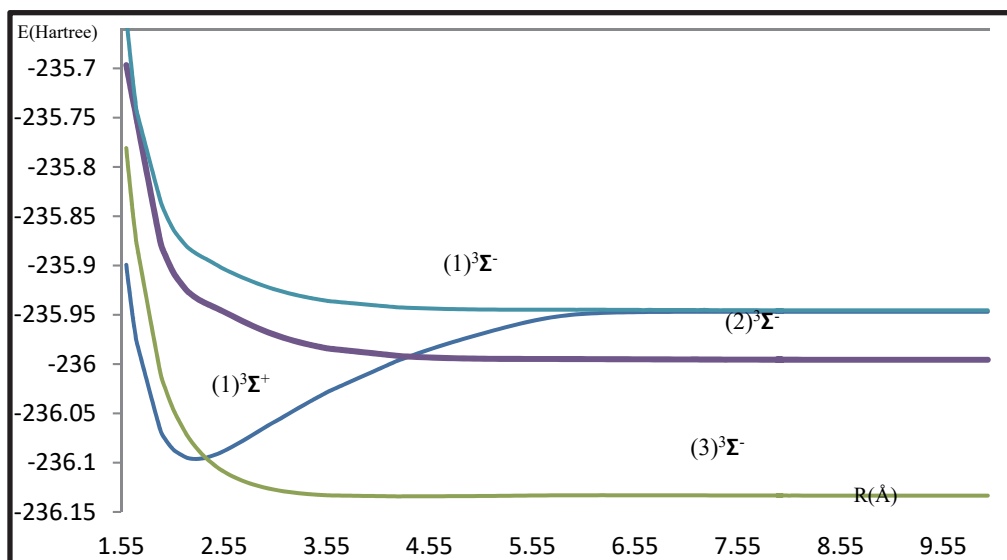
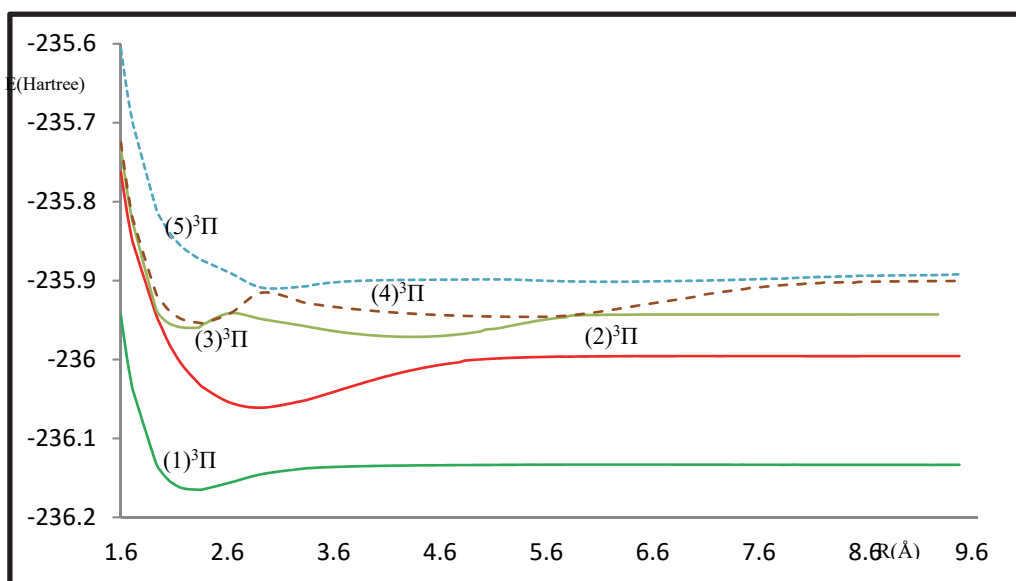Figure 3. Potential Energy Curves of the $^3\Sigma^{\pm}$ States of the Molecule ZnS

Figure 4. Potential Energy Curves of the $^3\Pi$ States of the Molecule ZnS

The spectroscopic constants ω_e, T_e, and B_e have been obtained by calculating points around the internuclear distance at equilibrium R_e. Table 1 illustrates the spectroscopic constants for some lowest singlet and triplet electronic states of ZnS diatomic molecule. The obtained results are compared with other available studies (Peterson, Spheler, & Singleton 2007), (Peterson, Spheler, & Singleton 2007 -CCSD(T)), (Chamboud 2008), (Raptis, Papadopoulos, Sadlej, 1999), (Jensen, Roos, & Ryde 2007), (Boldyrev, & Simsons 1997), (Bauschlicher, & Partridge .H 2001), (Dolg, Wedig, Stoll, & Preuss, 1987), and (Kullie, Zhang, Kolb, & Kolb, 2006).This comparison of the values is also shown in the given table.

Table 1. The Spectroscopic Constant of Diatomic Molecule ZnS

State	T_e cm^{-1}	$\Delta T_e/T_e$ %	R_e Å	$\Delta R_e/R_e$ %	B_e cm^{-1}	$\Delta B_e/B_e$ %	ω_e cm^{-1}	$\Delta\omega_e/\omega_e$ %
$X^1\Sigma^+$	0.0[a] 0.0[b] 0.0[c] 0.0[d] 0.0[e] 0.0[f] 0.0[g] 0.0[i] 0.0[j] 0.0[k]		2.106 2.046 3.886 3.87 3.92 2.12 3.91 2.083 2.048 2.074	2.93 45.80 45.58 46.27 0.66 46.1 1.10 2.83 1.54	0.1766		421.1 459.4 472.7 447.0 434.0 478.0 447.0	8.33 10.91 5.79 2.97 11.90 5.79
$(1)^3\Pi$	1646.45[a] 3840.00[b] 3980.00[c] 2258.00[g] 1797.70[i] 2334.80[j] 1141.80[k] 2257.68[l]		2.29 2.22 2.23 2.25 2.30 2.22 2.25	3.05 2.69 1.77 0.43 3.05 1.77	0.1491		305.69 343.8 347.00 329.00 287.00 349.00 329.00	11.08 11.90 7.08 6.51 12.40 7.08
$(2)^1\Sigma^-$	3243.03[a]		2.17		0.1656		388.11	
$(1)^1\Pi$	4464.00[a] 6888.00[c]		4.27 4.21	1.42	0.1656		351.82 363.80	3.29
$(1)^3\Sigma^+$	9375.03[a] 9696.36[i] 9864.47[j] 7462.84[k] 8798.25[l]		4.70 6.04 4.52 4.62	22.18 3.98 1.73	0.3701		271.57 7.00 20.00 18.00	100 100 100
$(2)^3\Sigma^+$	16778.1[a] 18539.4[i] 18340.7[j] 16937.4[k] 17899.3[l]		2.27 2.25 2.21 2.22	0.88 2.71 2.25	0.1517		324.68 309.00 336.00 335.00	5.07 3.36 3.08
$(2)^3\Pi$	24479.86[a]		2.89		0.9350		226.53	
$(3)^3\Pi$	46551.32[a]		3.33		0.7028		705.09	
$(3)^3\Sigma^-$	52520.27[a]		2.63		0.1129		221.19	
$(4)^3\Sigma^-$	54313.69[a]		2.63		0.1130		207.91	
$(4)^1\Pi$	54509.71[a]		2.49		0.1257			
$(2)^1\Delta$	64438.19[a]		2.55		0.1199		217.88	

[a]Present Work, [b](Peterson, Spheler, & Singleton, 2007), [c](Peterson, Spheler, & Singleton, 2007 - CCSD(T)), [d](Chamboud 2008), [e](Raptis, Papadopoulos, & Sadlej, 1999), [f](Jensen, Roos, & Ryde, 2007), [g](Boldyrev, & Simsons, 1997), [i](Bauschlicher,& Partridge, 2001), [j](Dolg, Wedig, Stoll, & Preuss, 1987), [k](Kullie, Zhang, Kolb, & Kolb, 2006).

By examining the given data, you notice that $^1\Sigma^+$ is the lowest electronic state of the diatomic molecule ZnS followed by $^3\Pi$ and $^1\Pi$ respectively. These states are close to each other (Chamboud 2008). For ZnS molecule the three states, $^1S^+$, ^3P and $^3S^+$ have short bond lengths and high frequencies and therefore they are chemically bound, while the $^3S^-$ state is of long bond and very low vibrational frequency. The $^1\Sigma^+$ is known always as shorter equilibrium band energy dissociation and larger dipole moment compared to those of $^3\Pi$ where state $^1\Sigma^+$ is stabilized relative to $^3\Pi$ (Chamboud 2008). The $^1S^+$ state was concluded as ground electronic state with r_e (the internuclear distance) = 2.106 Å and w_e (the harmonic frequency) =421.15 cm^{-1} which are compatible with other studies performed before and acceptable with percentage 2.9%, 0.66%, 1.1%, 2.8%, and 1.5% relative to some studies with respect to r_e. Similarly for ω_e it is compatible with some studies with percentage 2.9%, 5.7%, 7.1%, and 8.3%. And those the first exited state ^3P are calculated to be r_e= 2.29 Å and w_e= 305.69 cm^{-1} which are also in agree with those obtained in previous studies with percentage 0.5%, 1.4%, 1.7%, and 2.6% relative to r_e and

6.5%, and 7% with respect to ω_e. The sulfur atoms correlate in their ^3P ground electronic state with the ground electronic state of Zn to form $^3S^-$ states, not the singlet $^1S^+$ ground state. By comparing r_e and ω_e values - 4.27Å and 351.82 cm^{-1} respectively - of $^1\Pi$ with values performed by other studies, the results are compatible by 1.4% and 3.2% respectively. In case of $(1)^3\Sigma^-$, r_e shows compatibility with other studied by 1.5% and 3.9% while ω_e shows a big difference with results of other studies, whereas the $(2)^3\Sigma^-$ shows a good compatible with other studies by 0.75%, 1.9%, and 2.4% for r_e and 3%, 3.3%, and 5% for ω_e. The other electronic states are not compared to the fact that they r studied for the first time. By proposing the comparison for T_e we will see some compatible results with good percentage such that: $^3\Pi$ agrees by 8.4%, $(1)^3\Sigma^-$ and $(2)^3\Sigma^+$ agree with other results by 3.3% and 0.94% respectively. Other electronic states like $^1\Pi$ show a big disagreement with the only result performed by 35% as well as $^3\Pi$ which shows also a big disagreement with a mentioned study by 58%. The rest of states are compared since as it was mentioned before are being studied for the first time. According to the rotational constant B_e, no comparison are done since it is not calculated by other studies. One can notice that our calculated values of the spectroscopic constants are in better agreement with experimental data then the theoretical values given in literature for these constants. With this agreement with literature values, we can predict the accuracy of the spectroscopic constants of the new electronic states investigated for the first time in the present work.

3.2 Static Dipole Moment

By taking the Zn atom at the origin and sulfur atom along the internuclear Z-axis, we present in Figs (5-6-7-8) the calculated values of the static dipole moment in term of the internuclear distance R.
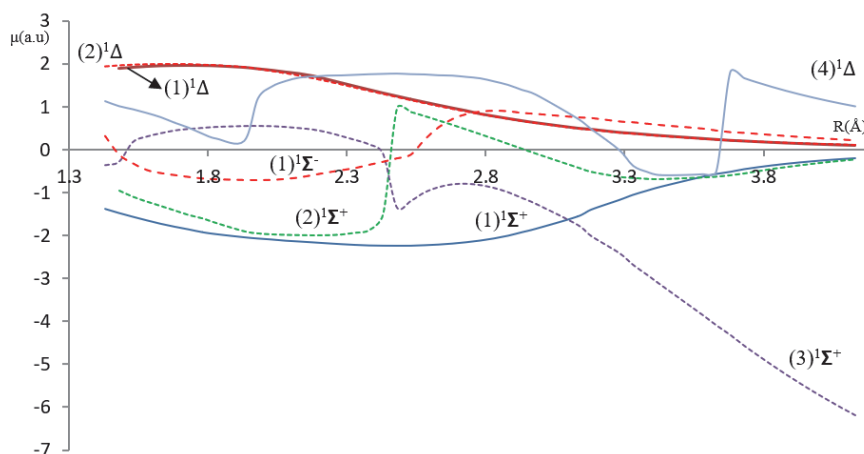

Figure 5. Static Dipole Curves of the Electronic States $^1\Sigma^{\pm}$, and $^1\Delta$ of the Molecule ZnS
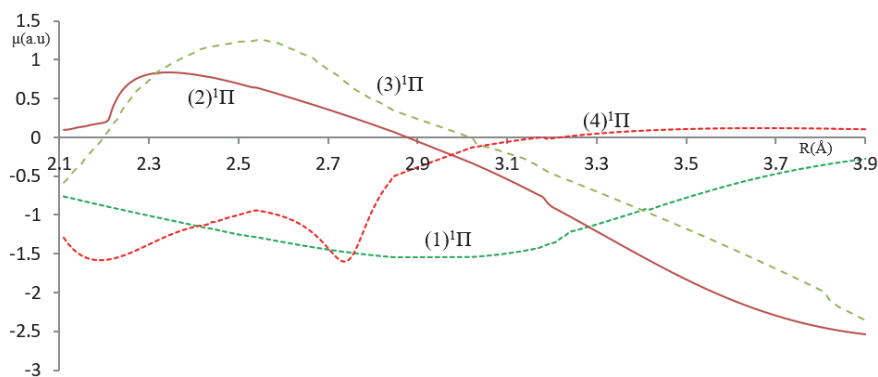

Figure 6. Static Dipole Curves of the Electronic States $^1\angle$ of the Molecule ZnS
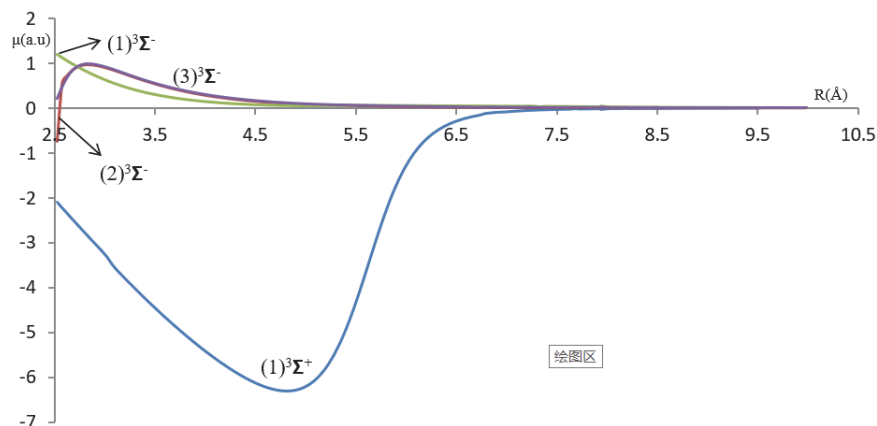
Figure 7. Static Dipole Curves of the Electronic States $^3\Sigma^\pm$ of the Molecule ZnS.
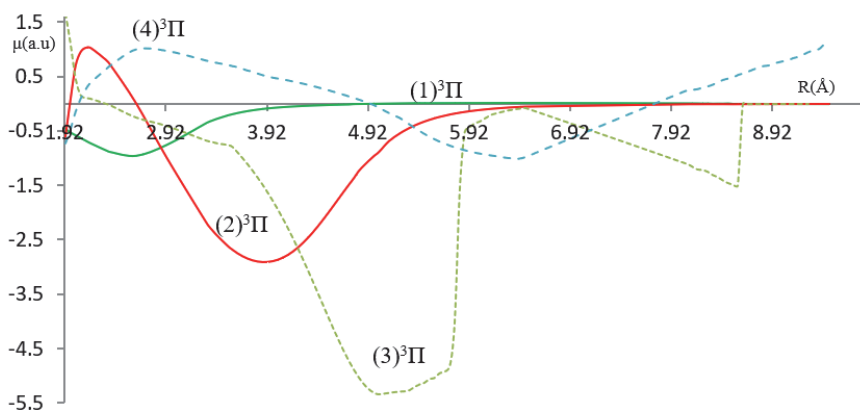

Figure 8. Static Dipole Curves of the Electronic States $^3\Pi$ of the Molecule ZnS.

The dipole value of the $^1S^+$ state is much higher than that of the two P states, which lie somehow above that of the $^3S^-$ state. Except for the dipole moment of the ^1P state, these values vary little with the inter-atomic distance (Chamboud 2008). The investigation of these curves is mainly used to discuss the bond nature, the polarity of the states and their interactions. As the internuclear distance increases one can notice three types of the DMC's for the singlet, triplet and quintet electronic states: curves in the positive region which are corresponding to an ionic structure of $Zn^{\delta-}S^{\delta+}$ type, curves in the negative region which are corresponding to an ionic structure of $Zn^{d+}S^{d-}$ type, and curves passing from one region to another by changing the ionic structure. It is noticed that at large internuclear distances, the dipole moment curves of all the investigated electronic states tend smoothly to zero which is theoretically the correct behavior for a molecule that dissociates into natural fragments. The sharp change in the directions of the DM curves indicate an avoided crossing of the potential energy curves at the same position of the internuclear distance where the polarity of the atoms is reversed (Atkins & Friedman). From this agreement, we can confirm the validity and the accuracy of the calculation of the studied excited electronic states.

It is known that the canonical functions approach can replace the radial Schrödinger equation (Kobeissi, Korek, & Dagher 1989), and (Korek 1999) where the eigenvalues E_v, and the rotational constants B_v have been calculated for the electronic states $(1)^3P$ and $(1)^3S^+$. These values are given in Table 2.

Table 2. The Eigenvalue E_v, and the Rotational Constant B_v of the Molecule ZnS.

State	V	$E_v(cm^{-1})$	$B_v \times 10^2$ (cm^{-1})
	0	164	16.77
	1	489	16.536

	2	809	16.388
	3	1124	16.249
	4	1433	16.104
	5	1737	15.981
	6	2035	15.943
	7	2326	16.137
	8	2612	16.617
	9	2890	15.279
	10	3162	15.1
	11	3427	14.915
	12	3685	14.724
	13	3936	14.53
$(1)^3\Pi$	14	4179	14.356
	15	4415	14.288
	16	4641	14.499
	17	4858	15.006
	18	5066	15.309
	19	5262	9.359
	20	5448	23.647
	21	5623	10.533
	22	5786	160.918
	23	5937	13.705
	24	6075	6.388
	25	6200	32.162
	26	6313	14.111
	0	177	16.8872
	1	519	16.8051
	2	854	16.6824
	3	1190	16.6229
	4	1519	16.5143
	5	1848	16.4259
	6	2174	16.3458
	7	2499	16.2474
	8	2821	16.1613
	9	3140	16.0593
	10	3457	15.9611
$(1)^3\Sigma^+$	11	3771	15.8657
	12	4082	15.7654
	13	4391	15.6692
	14	4698	15.5691
	15	5003	15.4653
	16	5305	15.362
	17	5605	15.2522
	18	5903	15.1344
	19	6199	15.0078
	20	6492	14.8649
	21	6784	14.7024
	22	7073	14.5212
	23	7359	14.3194
	24	7643	14.0992
	25	7924	13.8691
	26	8202	13.6377
	27	8476	13.4175
	28	8746	13.2303

29	9014	13.0954
30	9281	13.0085
31	9546	12.9417
32	9811	12.8689
33	10074	12.7819
34	10335	12.6821
35	10594	12.5678
36	10851	12.4377
37	11107	12.299
38	11361	12.1639
39	11613	12.0434
40	11864	11.9426
41	12112	11.8597
42	12359	11.7867
43	12604	11.7147
44	12848	11.6352
45	13089	11.543
46	13329	11.438
47	13568	11.326
48	13804	11.215
49	14039	11.1131
50	14272	11.024
51	14504	10.9482
52	14733	10.8808
53	14962	27.4959
54	15188	10.7447
55	15413	9.9711
56	15636	74.6
57	15858	26.3

To draw connections among the different investigated data, we will refer to the following spectroscopic formulas (Herzberg 1950)

$$E_v = \omega_e(v+1/2) - \omega_e x_e(v+1/2)2 + ..$$

$$B_v = B_e - \alpha(v+1/2) ..$$

For $v = 0$ of the electronic states $(1)^3\Pi$ and $(1)\ ^3\Sigma^+$, with approximation to the first term, implies that $\omega_e = 328$ cm^{-1} is a constant whose value is in good accordance to $\omega_e = 312$ cm^{-1}, and $\omega_e = 354$ cm^{-1} is close to $\omega_e = 340$ cm^{-1} respectively. Also, the value of $B_e = 0.1682$ cm^{-1} is close to the value of $B_e = 0.1491$ cm^{-1}, and $B_e = 0.1679$ cm^{-1} is close to $B_e = 0.1493$ cm^{-1} respectively. No comparison with other data since they given here for the first time.

4. Conclusion

The ab-*initio* MRCI+Q calculation of permanent dipole moment and the potential energy curves was investigated for 21 singlets, and triplet electronic states for diatomic molecule zinc sulfide ZnS. The study includes plots of these curves, and the spectroscopic constants R_e, ω_e, T_e, and B_e of the investigated electronic states which are compared with the results of other studies when available. The spectroscopic constants for 7 states are given here for the first time. The confirmation of these theoretical investigated data can be done by a future experiment for these electronic states of the molecule ZnS.

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