

# Ab initio study of the ground and excited states of the zinc sulfide diatomic system, ZnS

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## ABSTRACT

The electronic structure of the ground and excited states of the ZnS species has been investigated by variational multireference and, in some cases, coupled-cluster techniques employing augmented basis sets of quintuple- $\zeta$  quality. Full potential energy curves are reported for 18 states. The nature of the bonding for the lowest electronic states is discussed in some detail.

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## 1. Introduction

Zinc sulfide, ZnS, is a white to yellow-colored powder or crystal with very interesting optical [1] and electrical [2,3] properties and a variety of technological applications. The bulk properties of ZnS could be better understood on the basis of the electronic and bonding characteristics of the parent diatomic ZnS molecule. As an example we mention a recent theoretical work by Chambaud et al. [4], which established a correlation between the electronic structure of molecular ZnS and the piezoelectric properties of solid ZnS. However, work on this diatomic sulfide, either experimental or theoretical, is rather limited.

In 1933, Sen-Gupta [5] studied the absorption spectrum of ZnS in the  $\lambda$  7000–1900 region and deduced a rough estimate of  $\sim 98$  kcal/mol for the dissociation energy of this molecule. Two subsequent mass spectroscopic studies in 1963 and 1965 yielded  $D_0(\text{ZnS}) \leq 50$  kcal/mol [6] and  $D_0(\text{ZnS}) = 48.0 \pm 3.0$  kcal/mol [7], respectively. It is rather enigmatic that since these last studies and for 44 years no experimental work was reported on this diatomic species until, in 2009, Zack and Ziurys [8] presented a paper on the pure rotational spectrum of ZnS ( $X^1\Sigma^+$ ). These authors determined the equilibrium bond length and some spectroscopic constants for the ground state of the zinc sulfide. Also, an estimate of  $D_e \sim 3.12$  eV was calculated assuming a Morse potential energy curve.

Now, the first theoretical ab initio investigation of the ZnS electronic structure was published in 1986 by Bauschlicher and Langhoff [9]. They carried out single point CI and CPF calculations with limited basis sets for the first four electronic states of ZnS. They showed that the ground state is of  $^1\Sigma^+$  symmetry with two,  $^3\Pi$  and  $^1\Pi$ , states lying slightly higher. They also, computed a binding energy of 1.22 eV for the ground state which was significantly smaller than the corresponding experimental values. During the

next years, ZnS was included in several theoretical ab initio or DFT studies [4,10–15]. The most reliable among them are those by Peterson et al. [15] and by Chambaud et al. [4]. They used multireference methods in conjunction with large correlation consistent basis sets and focused on two states, namely,  $X^1\Sigma^+$  and  $a^3\Pi$ . In both works parts of the potential energy curves were computed, as well as, equilibrium bond lengths, dipole moments, and spectroscopic constants. Peterson et al. studied the effects of the spin-orbit coupling on the  $a^3\Pi$  state and they also reported dissociation energies,  $D_0$ . Interestingly, these authors studied all group 12 metal chalcogenides MX with M = Zn, Cd, Hg and X = O, S, Se, Te, Po. A useful review on previous works concerning this category of diatomics can be found in their paper.

In the present theoretical investigation we employ multireference (MRCI) and coupled cluster [RCCSD(T)] methods combined with extensive basis sets in order to study the structure and bonding of all electronic states of ZnS, stemming from the first four, Zn( $^1S$ ) + S( $^3P$ ,  $^1D$ ,  $^1S$ ) and Zn( $^3P$ ) + S( $^3P$ ), asymptotic channels within an energy range of approximately 4 eV [16]. In particular, and for the first time, full potential energy curves (PEC) have been constructed for a total of 18 states, 13 bound and five of repulsive nature. For all bound states, we report total energies, binding energies, common spectroscopic constants ( $r_e$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $a_e$ ,  $\bar{D}_e$ ), dipole moments and energy separations.

## 2. Computational outline

For the Zn atom the augmented quintuple- $\zeta$  correlation consistent basis set was used, aug-cc-pV5Z = (29s21p13d5f4g3h2i) [17], whereas for the S atom the corresponding basis, aug-cc-pV5Z = (21s13p5d4f3g2h) [18] was employed. Both sets were generally contracted to [10s9p7d5f4g2h2i]<sub>Zn</sub> 8s7p5d4f3g2h/s] = A5 $\zeta$ , a total of 333 spherical GAUSSIANS.

We have followed two methods of calculation, the complete active space self-consistent field (CASSCF) + single + double

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replacements (CASSCF + 1 + 2 = MRCI), and the restricted coupled cluster with single + double + quasi-perturbative triple replacements [RCCSD(T)] [19–21]. In the MRCI calculations the reference space was defined by allotting eight  $[4s^2(\text{Zn}) + 3s^2(\text{S}) + 3p^4(\text{S})]$  electrons to eight orbitals corresponding to the four  $(4s_{\text{Zn}}, 4p_{\text{Zn}}) +$  four  $(3s_{\text{S}}, 3p_{\text{S}})$  valence space of the ZnS system. Valence internally contracted (ic) [22,23] MRCI wave functions were calculated through single + double excitations out of the reference space including, however, the  $3d^{10}$  electrons of Zn. The MRCI spaces range from  $\sim 7 \times 10^8$  to  $\sim 1.3 \times 10^9$  configuration functions (CF) and were internally contracted to  $\sim 8 \times 10^6 - 16 \times 10^6$  CFs. Scalar relativistic effects were computed through the 8th order Douglas–Kroll–Hess (DKH) method [24–26]. For the DKH calculations the Zn basis set was recontracted appropriately [17] while the S basis was left uncontracted. The basis set superposition errors (BSSE) are quite small and are not considered. For instance, at the MRCI/A5 $\zeta$  level the BSSE for the  $X^1\Sigma^+$  state was  $\sim 0.1$  kcal/mol. To take into account the size non-extensivity errors (SNE) of  $\sim 25$  mE $_h$  for all channels, the Davidson correction (MRCI + Q) [27,28] was applied, which reduced the SNE to  $\sim 6$  mE $_h$ .

All calculations were performed with the MOLPRO 2006.1 program [29].

### 3. Results and discussion

Considering the first asymptotic energy channels of the Zn + S system, the following molecular ZnS electronic states are expected:

- $\text{Zn}(^1\text{S}) + \text{S}(^3\text{P}) \rightarrow \text{ZnS } [^3\Sigma^-, ^3\Pi]$
- $\text{Zn}(^1\text{S}) + \text{S}(^1\text{D}) \rightarrow \text{ZnS } [^1\Sigma^+, ^1\Pi, ^1\Delta]$
- $\text{Zn}(^1\text{S}) + \text{S}(^1\text{S}) \rightarrow \text{ZnS } [^1\Sigma^+]$
- $\text{Zn}(^3\text{P}) + \text{S}(^3\text{P}) \rightarrow \text{ZnS } [^{5,3,1}\Sigma^+, ^{5,3,1}\Sigma^-(x2), ^{5,3,1}\Pi(x2), ^{5,3,1}\Delta]$

i.e. a total of 24 states. All quintets stemming from the asymptote (d) are expected to be repulsive and are not considered any further. Figure 1 displays PECs of 18 states at the MRCI/A5 $\zeta$  level. As a first general remark, we mention the strong resemblance with the corresponding PEC diagram of the isovalent ZnO system, published last year [30]. All curves of Figure 1 give asymptotic energy gaps in relatively good agreement with experimental data [16]. Our computed (vs. experimental J-averaged) values in  $\text{cm}^{-1}$ , are  $\Delta E[\text{S}(^1\text{D}) \leftarrow \text{S}(^3\text{P})] = 9548(9042.8)$ ,  $\Delta E[\text{S}(^1\text{S}) \leftarrow \text{S}(^3\text{P})] = 22026(22179.9)$ , and  $\Delta E[\text{Zn}(^3\text{P}) \leftarrow \text{Zn}(^1\text{S})] = 30430(32696)$  at the MRCI/A5 $\zeta$  level of theory.

For all bound states numerical equilibrium results are collected in Table 1. In what follows we discuss the manifold of bound states in ascending order.

#### 3.1. $X^1\Sigma^+$

As we can see from Figure 1, the ground state of ZnS is of  $^1\Sigma^+$  symmetry and correlates adiabatically to  $\text{Zn}(^1\text{S}) + \text{S}(^1\text{D})$ , channel (b). The leading equilibrium MRCI configuration and the Mulliken atomic populations are:

$$|X^1\Sigma^+\rangle \approx 0.92 \left| 1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2 \right\rangle$$

$$4s^{1.12} 4p_z^{0.12} 4p_x^{0.20} 4p_y^{0.20} /_{\text{Zn}(+0.36)} 3s^{1.78} 3p_z^{0.95} 3p_x^{1.81} 2p_y^{1.81} /_{\text{S}(-0.36)}$$

where, for simplicity, only valence electrons are counted. Now, considering the atomic  $\text{Zn}(^1\text{S}) + \text{S}(^1\text{D})$  fragments, the only bonding interaction between them can be depicted by the valence bond–Lewis (vbl) diagram of Scheme 1 here only the first term of the atomic  $|^1\text{D}; M_L = 0\rangle = \frac{1}{\sqrt{6}}(2|p_x^2 p_y^2\rangle - |p_x^2 p_z^2\rangle - |p_y^2 p_z^2\rangle)$  wavefunction of S is shown.

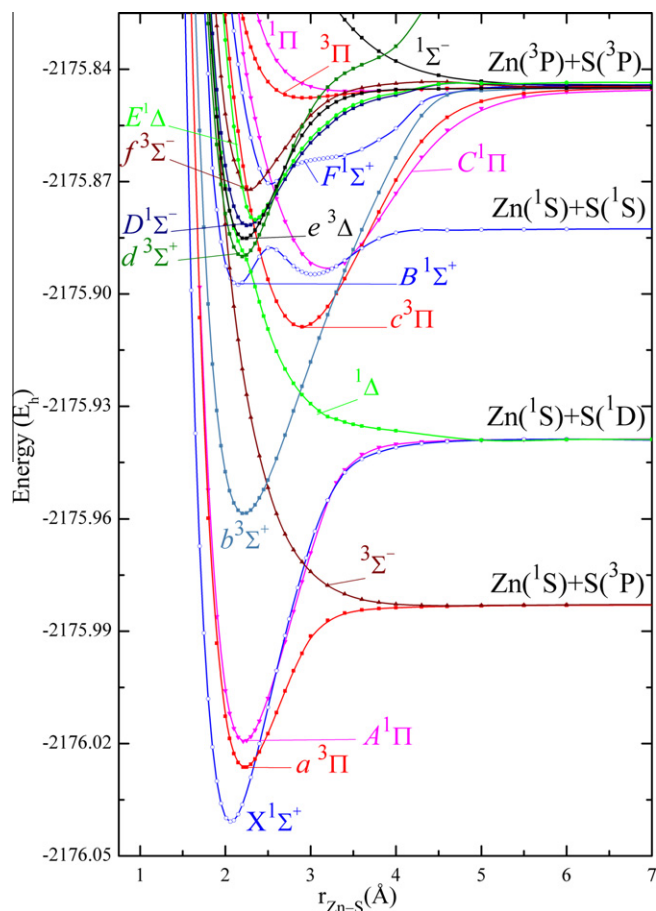


Figure 1. Potential energy curves of ZnS at the MRCI/A5 $\zeta$  level of theory.

This vbl diagram clearly implies a Zn  $\rightarrow$  S dative bond which can hardly justify a ZnS binding energy of  $\sim 62$  kcal/mol (Table 1). However, at equilibrium we see that a population of  $\sim 0.52$  e is promoted to the Zn p system. The in situ Zn distribution  $4s^{1.12} 4p^{0.52}$  suggests that the  $\text{Zn}(^3\text{P})$  excited state could be involved in the formation of the  $X^1\Sigma^+$  ground state of ZnS. According to the vbl diagram shown in Scheme 2, the  $\text{Zn}(^3\text{P}) + \text{S}(^3\text{P})$  interaction leads to a, formally, triply bonded (with one  $\sigma$  and two  $\pi$  bonds)  $\text{ZnS } ^1\Sigma^+$  state.

If the ground state is to originate diabatically from the asymptote (d), an intrinsic bond strength of approximately 125 kcal/mol would be required. The latter is fully justified by the bonding mechanism of Scheme 2. On the other hand, the shapes of the two higher, B and F,  $^1\Sigma^+$  states (Figure 1), stemming from channels (c) and (d), are indicative of the presence of some avoided crossings in the region of  $r_{\text{Zn-S}} = 3 - 4$  Å.

As it can be seen from Table 1, the calculated bond distance is in excellent agreement with experiment [8] after taking into account scalar relativistic effects at both levels, MRCI + Q and RCCSD(T). For the binding energy our results converge to  $D_0 = 61.0 \pm 1.5$  kcal/mol (upper and lower values corresponding to the RCCSD(T) + DKH and MRCI + DKH + Q) with respect to the  $\text{Zn}(^1\text{S}) + \text{S}(^1\text{D})$  adiabatic asymptote. This value is in agreement with the 60.7 kcal/mol theoretical value by Peterson et al. [15]. We believe that the  $D_0 \sim 72$  kcal/mol value calculated by Zack and Ziurys [8] on the basis of spectroscopic data but assuming a Morse potential, is rather excessive. The earlier experimental upper limit of  $D_0 \leq 50$  kcal/mol [6] and the  $D_0 = 48.0 \pm 3.0$  kcal/mol value [7] are with respect to the ground state fragments  $\text{Zn}(^1\text{S}) + \text{S}(^3\text{P})$ . We believe that these results must be wrong because they were deduced by assuming,

**Table 1**  
Total energies  $E$  ( $E_h$ ), bond distances  $r_e$  (Å), dissociation energies  $D_0$  (kcal mol<sup>-1</sup>), harmonic and anharmonic frequencies  $\omega_e$ ,  $\omega_e x_e$  (cm<sup>-1</sup>), rotational–vibrational coupling constants  $\alpha_e \times 10^3$  (cm<sup>-1</sup>), centrifugal distortion  $D_e \times 10^7$  (cm<sup>-1</sup>), dipole moments  $\mu$  (D), and energy separations  $T_0$  (eV) of the <sup>64</sup>Zn<sup>32</sup>S molecule.

Method <sup>a</sup>	$-E$	$r_e$	$D_0^b$	$\omega_e$	$\omega_e x_e$	$\alpha_e$	$D_e$	$\langle \mu \rangle / \mu_{FF}^c$	$T_0^b$
<b>X<sup>1</sup>Σ<sup>+</sup>d</b>									
MRCI	2176.041029	2.066	63.1	457	1.98	1.07	1.17	5.70/5.51	0.000
MRCI + Q	2176.09820	2.062	62.0	461	1.99	1.10	1.19	/5.47	0.000
MRCI + DKH	2193.595313	2.054	55.6	458	1.62	1.02	1.25	5.49/5.39	0.000
MRCI + DKH + Q	2193.65254	2.047	59.6	461	1.50	1.00	1.25	/5.32	0.000
RCCSD(T)	2176.123878	2.062	64.5	458	1.67	1.07	1.05	/5.33	0.000
RCCSD(T) + DKH	2193.679808	2.048	62.5	461	2.12	1.06	1.27	/5.11	0.000
Expt.		2.0464 <sup>e</sup>	≤50 <sup>f</sup> 48.0 ± 3.0 <sup>g</sup> 72 <sup>e</sup>	459 <sup>e</sup>	2.09 <sup>e</sup>	1.086 <sup>e</sup>	1.28 <sup>e</sup>		0.000
<b>a<sup>3</sup>Π<sup>h</sup></b>									
MRCI	2176.026389	2.229	26.7	356	1.66	1.00	1.25	1.92/1.97	0.392
MRCI + Q	2176.08119	2.233	25.4	350	1.71	1.01	1.29	/1.97	0.456
MRCI + DKH	2193.579984	2.220	24.0	354	1.86	1.07	1.32	1.84/1.85	0.410
MRCI + DKH + Q	2193.63586	2.223	24.2	347	1.87	1.09	1.40	/1.85	0.447
RCCSD(T)	2176.107908	2.236	25.0	345	1.47	1.03	1.36	/1.90	0.428
RCCSD(T) + DKH	2193.663542	2.224	22.9	342	1.85	1.10	1.41	/1.86	0.436
<b>A<sup>1</sup>Π<sup>d</sup></b>									
MRCI	2176.019399	2.220	50.1	380	1.23	0.79	1.15	2.10/2.21	0.584
MRCI + Q	2176.07273	2.218	46.4	374	1.30	0.84	1.20	/2.14	0.682
MRCI + DKH	2193.572256	2.206	49.1	382	1.71	0.87	1.15	2.02/2.09	0.622
MRCI + DKH + Q	2193.62680	2.205	45.1	376	1.66	0.91	1.22	/2.12	0.695
<b>b<sup>3</sup>Σ<sup>+</sup>i</b>									
MRCI	2175.958594	2.221	68.2	338	1.33	0.95	1.45	2.56/2.77	2.235
MRCI + Q	2176.01463	2.215	71.0	338	1.34	0.98	1.46	/2.92	2.266
MRCI + DKH	2193.508814	2.212	68.0	337	1.34	0.98	1.52	2.56/2.97	2.347
MRCI + DKH + Q	2193.56569	2.205	70.8	338	1.35	1.00	1.53	/2.91	2.355
RCCSD(T)	2176.040401	2.214	71.5	337	1.33	0.99	1.46	/2.99	2.264
RCCSD(T) + DKH	2193.592149	2.202	71.2	337	1.36	1.01	1.51	/2.98	2.378
<b>c<sup>3</sup>Π<sup>i</sup></b>									
MRCI	2175.908774	2.896	39.8	219	0.52	1.09	0.70	1.51/2.16	3.584
MRCI + Q	2175.96977	2.892	43.9	222	0.60	0.82	0.70	/2.40	3.480
<b>B<sup>1</sup>Σ<sup>+</sup>j</b>									
MRCI <sup>k</sup>	2175.897536	2.149	8.8	377	2.21	1.21	1.22	3.21/3.29	3.900
MRCI + Q <sup>k</sup>	2175.96137	2.140	13.0	385	3.21	1.41	1.30	/3.16	3.718
MRCI <sup>l</sup>	2175.894776	3.031	7.4	160	0.75	0.22	1.07	0.14/0.36	3.960
MRCI + Q <sup>l</sup>	2175.95449	2.976	9.0	160	1.16	0.29	1.19	/0.40	3.891
<b>C<sup>1</sup>Π<sup>i</sup></b>									
MRCI	2175.893782	3.191	30.4	187	0.46	-0.02	0.54	1.64/2.46	3.990
MRCI + Q	2175.95518	3.166	34.6	192	0.40	-0.04	0.54	/2.70	3.876
<b>d<sup>3</sup>Σ<sup>m</sup></b>									
MRCI	2175.890020	2.205	55.6	375	1.90	1.00	1.25	1.71/1.82	4.103
MRCI + Q	2175.95076	2.199	57.9	377	1.85	1.05	1.24	/1.79	3.882
<b>e<sup>3</sup>Δ<sup>i</sup></b>									
MRCI	2175.885258	2.227	24.8	355	2.10	1.10	1.27	1.46/1.49	4.232
MRCI + Q	2175.94614	2.216	28.8	363	1.94	1.03	1.26	/1.53	4.131
<b>D<sup>1</sup>Σ<sup>-i</sup></b>									
MRCI	2175.881762	2.264	23.1	307	3.99	1.94	1.57	0.80/1.41	4.325
MRCI + Q	2175.94217	2.239	26.5	343	4.77	1.72	1.36	/1.50	4.239
<b>E<sup>1</sup>Δ<sup>i</sup></b>									
MRCI	2175.880179	2.350	22.4	453	8.58	1.00	0.56	0.13/0.71	4.375
MRCI + Q	2175.94096	2.312	26.0	452	6.10	1.00	0.61	/0.90	4.279
<b>f<sup>3</sup>Σ<sup>i</sup></b>									
MRCI	2175.872202	2.272	16.7	320	3.17	1.42	1.40	0.44/1.36	4.584
MRCI + Q	2175.93446	2.244	22.3	349	2.61	1.27	1.26	/1.59	4.449
<b>F<sup>1</sup>Σ<sup>+</sup>i</b>									
MRCI	2175.870651	2.539	16.85	354	14.7	2.05	0.54	0.54/0.02	4.636
MRCI + Q	2175.93172	2.524	20.67	387	11.8	1.06	0.56	/0.04	4.530

<sup>a</sup> +Q and DKH refer to Davidson correction and Douglas–Kroll–Hess scalar relativistic corrections of the 8th order, respectively.

<sup>b</sup> Zero-point energy obtained by numerically solving the rovibrational Schrödinger equation.

<sup>c</sup>  $\langle \mu \rangle$  calculated as an expectation value,  $\mu_{FF}$  through the finite field approach; field strength  $5 \times 10^{-5}$  a.u.

<sup>d</sup>  $D_0$  with respect to Zn(<sup>1</sup>S) + S(<sup>1</sup>D).

<sup>e</sup> Ref. [8].

<sup>f</sup> Ref. [6].

<sup>g</sup> Ref. [7].

<sup>h</sup>  $D_0$  with respect to Zn(<sup>1</sup>S) + S(<sup>3</sup>P).

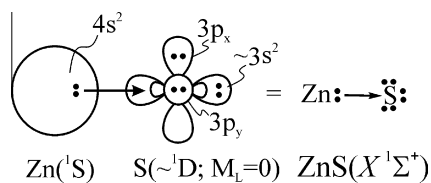
<sup>i</sup>  $D_0$  with respect to Zn(<sup>3</sup>P) + S(<sup>3</sup>P).

<sup>j</sup>  $D_0$  with respect to Zn(<sup>1</sup>S) + S(<sup>1</sup>S).

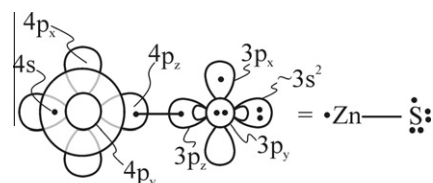
<sup>k</sup> Global minimum.

<sup>l</sup> Local minimum.

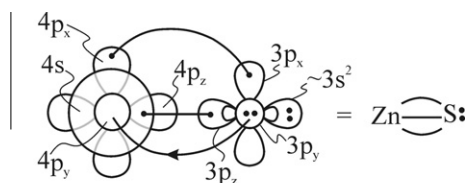
<sup>m</sup>  $D_0$  with respect to Zn(<sup>3</sup>P) + S(<sup>1</sup>D).



Scheme 1.



Scheme 3.



Scheme 2.

for ZnS,  $r_e$  and  $\omega_e$  values which were not correct. Our corresponding calculated number is 35 kcal/mol at the MRCI + DKH + Q level. Now, concerning the dipole moment, the recommended finite field value is  $\mu_{FF} = 5.2 \pm 0.1$  D in complete agreement with the theoretical values of Refs. [4,15]. This high dipole moment is almost identical with the  $5.3 \pm 0.1$  D value computed for ZnO [30] and denotes some admixture of ionic character. No experimental value of the ZnS dipole moment exists in the literature.

Finally, we see from Table 1 that our computed  $\omega_e$ ,  $\omega_e x_e$ ,  $a_e$ , and  $\bar{D}_e$  spectroscopic constants compare nicely to the recent experimental data by Zack and Ziurys.

### 3.2. $a^3\Pi$

This is the first excited state of ZnS and correlates adiabatically to the ground state atomic fragments, Figure 1. However, it is clear that the combination of the Zn(<sup>1</sup>S;  $4s^2$ ) + S(<sup>3</sup>P;  $2s^2 2p^4$ ) electronic distributions can only result in a weak van der Waals interaction between the two atoms, which, in no way, can be as strong as  $\sim 24$  kcal/mol (Table 1). Here, again, the explanation lies in the involvement of the Zn(<sup>3</sup>P) excited state. The main equilibrium MRCI configuration ( $B_1$  component) and Mulliken populations of  $a^3\Pi$  are:

$$|a^3\Pi\rangle \approx 0.94 |1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle$$

$$4s^{1.17} 4p_z^{0.43} 4p_x^{0.05} 4p_y^{0.07} /_{Zn(+0.28)} 3s^{1.91} 3p_z^{1.49} 3p_x^{0.95} 2p_y^{1.93} /_{S(-0.28)}$$

These populations suggest the vBL diagram shown in Scheme 3, where the in situ Zn atom finds itself in its  ${}^3P(4s^1 4p^1)$  excited state. As we can see, the formation of a  $\sigma$  bond causes an electron transfer of  $\sim 0.4$  e from the Zn( $4s^1 4p^1$ ) distribution to the singly occupied  $3p_z$  orbital of the S atom. The interaction of the asymptotic configurations (a) and (d) gives rise to the adiabatic PECs  $a^3\Pi$  and  $c^3\Pi$ , Figure 1. Indeed, we were able to construct the corresponding diabatic curves which revealed a non-adiabatic crossing at  $r_{Zn-S} = 2.7$  Å. At this point, the populations of Zn 4s,  $4p_z$  and S  $3p_z$  change from 2.00, 0.00 and 1.00 e<sup>-</sup> to 1.39, 0.24 and 1.31 e<sup>-</sup>, respectively, to end up, at equilibrium, 1.17, 0.43 and 1.49 e<sup>-</sup>.

Equilibrium numerical results are reported on Table 1. There are no experimental data on the excited states of ZnS so any comparison with experiment is not possible. However, our recommended values of  $r_e = 2.225 \pm 0.007$  Å,  $D_0 = 24.0 \pm 1.0$  kcal/mol,  $\mu_{FF} = 1.85$  D,  $\omega_e = 345$  cm<sup>-1</sup>, and  $T_0 = 0.445 \pm 0.01$  eV, are in very good agreement with the recent theoretical results of Refs. [4,15].

### 3.3. $A^1\Pi$

The second excited state of ZnS is of  ${}^1\Pi$  symmetry and correlates adiabatically to the Zn(<sup>1</sup>S) + S(<sup>1</sup>D) atomic products. The equilibrium leading configuration and Mulliken atomic orbital distribution are

$$|A^1\Pi\rangle \approx 0.94 |1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle$$

$$4s^{1.10} 4p_z^{0.49} 4p_x^{0.03} 4p_y^{0.06} /_{Zn(+0.32)} 3s^{1.93} 3p_z^{1.48} 3p_x^{0.99} 2p_y^{1.92} /_{S(-0.32)}$$

almost identical to those of  $a^3\Pi$ . The bonding picture can be captured by the vBL diagram shown in Scheme 3 but with the  $4s^1 3p_x^1$  electrons coupled into a singlet. The  $A^1\Pi$  state diabatically correlates to Zn(<sup>3</sup>P) + S(<sup>3</sup>P) as does  $a^3\Pi$ . These two states have same bond lengths and their small energy separation corresponds to the spin flip of the two single electrons. Our recommended  $T_0 = 0.695$  eV value is much larger than  $T_e = 0.275$  eV calculated by Bauschlicher and Langhoff [9] and lower than  $T_e = 0.854$  eV by Chambaud et al. [4]. For the first time we report a binding energy,  $D_0 = 45$  kcal/mol, for the  $A^1\Pi$  state of ZnS. This value is almost twice the binding energy of  $a^3\Pi$  because it is calculated with respect to the Zn(<sup>1</sup>S) + S(<sup>1</sup>D) dissociation channel. However, the two states have similar binding energies with respect to their Zn(<sup>3</sup>P) + S(<sup>3</sup>P) diabatic asymptote.

### 3.4. $b^3\Sigma^+$

Next, but much higher than the bunch of the first three electronic states of ZnS, is the  $b^3\Sigma^+$  state. It has an energy separation of  $T_0 = 2.36 \pm 0.01$  eV from the ground state and, adiabatically, traces its lineage to the Zn(<sup>3</sup>P) + S(<sup>3</sup>P) atomic states, Figure 1. The main equilibrium and Mulliken populations are given below:

$$|b^3\Sigma^+\rangle \approx 0.93 |1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi_x^2 1\pi_y^2\rangle$$

$$4s^{0.93} 4p_z^{0.35} 4p_x^{0.14} 4p_y^{0.14} /_{Zn(+0.44)} 3s^{1.88} 3p_z^{0.84} 3p_x^{1.86} 2p_y^{1.86} /_{S(-0.44)}$$

These populations are very similar to those of the  $X^1\Sigma^+$  ground state. The bonding can be described by the vBL diagram shown in Scheme 2 but with the two electrons forming the  $\sigma$  bond uncoupled, to form a triplet, as indicated by the main MRCI configuration. Thus, the  $\sigma$  bond breaking in the ground state of ZnS leads to the formation of the  $b^3\Sigma$  excited state. A total of 0.44 e is transferred from Zn to S. The recommended equilibrium bond distance  $r_e = 2.204 \pm 0.002$  Å is slightly shorter than that calculated by Boldyrev and Simons [11] at the MP2/6-311++G(d,f) level. Of course, this bond is by  $\sim 0.1$  Å longer than that of  $X^1\Sigma^+$ , as a result of the  $\sigma$  bond rupture. The recommended  $D_0 = 71$  kcal/mol value was computed for the first time while, the  $\mu_{FF} = 2.95 \pm 0.04$  D dipole moment compares well with the 2.825 D QCISD/6-311++G value of Ref. [11].

3.5.  $c^3\Pi$ ,  $B^1\Sigma^+$ ,  $C^1\Pi$ ,  $d^3\Sigma^+$ ,  $e^3\Delta$ ,  $D^1\Sigma^-$ ,  $E^1\Delta$ ,  $F^3\Sigma^-$ ,  $F^1\Sigma^+$ 

All these states are located within a MRCI + Q energy window of  $T_0 = 3.4804.530$  eV. The  $B^1\Sigma^+$  and  $d^3\Sigma^+$  states correlate adiabatically to the  $Zn(^1S) + S(^1S)$  and  $Zn(^3P) + S(^1D)$  atomic channels, respectively, while the rest of them correlate to  $Zn(^3P) + S(^3P)$ .

All bound states stemming from the  $Zn(^3P) + S(^3P)$  asymptote have binding energies ranging from 43.9 ( $c^3\Pi$ ) to 20.7 kcal/mol ( $F^1\Sigma$ ), and  $\mu_{FF}$  dipole moments from 0.02 ( $F^1\Sigma$ ) to 2.70 D ( $C^1\Pi$ ), at the MRCI + Q level. Calculated spectroscopic constants for all states are listed in Table 1. On Figure 1, we have also reported PECs of three, essentially, repulsive ( $^3\Pi$ ,  $^1\Pi$ ,  $^1\Sigma$ ) states emerging from the same asymptotic channel. Note, however, that very shallow minima with  $D_e = 3.5$  and 1.8 kcal/mol, were detected on the  $^3\Pi$  and  $^1\Pi$  PECs at  $r_e = 2.860$  and 3.280 Å, respectively, at the MRCI + Q level.

Now, from Figure 1 we see that the  $B^1\Sigma^+$  state has a double minimum, which is the result of consecutive avoided crossings. Its global minimum is at  $r_{Zn-S} = 2.140$  Å with a binding energy of 13.0 kcal/mol at the MRCI + Q level. The two minima are separated by a 7 kcal/mol energy barrier, with respect to the global minimum, located at  $r_{Zn-S} = 2.550$  Å.

Finally, the  $d^3\Sigma^+$  state correlates to the doubly excited  $Zn(^3P) + S(^1D)$  atomic asymptote and has  $D_0 = 57.9$  kcal/mol at  $r_e = 2.199$  Å with  $\mu_{FF} = 1.80$  D at the MRCI + Q level of theory.

For all states discussed in this section, the leading configurations and total Mulliken charges on Zn ( $q_{Zn}$ ) are tabulated below:

$$\begin{aligned} |c^3\Pi\rangle &\approx 0.50 |1\sigma^2 2\sigma^1 3\sigma^2 1\pi_x^1 1\pi_y^2\rangle \\ &+ 0.68 |1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle \end{aligned} \quad (+0.24)$$

$$\begin{aligned} |c^1\Pi\rangle &\approx 0.54 |1\sigma^2 2\sigma^1 3\sigma^2 1\pi_x^1 1\pi_y^2\rangle + 0.60 |1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle \\ &+ 0.37 |1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^1 1\pi_y^2\rangle \end{aligned} \quad (+0.18)$$

$$\begin{aligned} |B^1\Sigma^+\rangle &\approx 0.60 |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^2 1\pi_y^2\rangle + 0.38 |1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2\rangle \\ &- 0.38 |1\sigma^2 2\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2\rangle - 0.38 |1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_y^1\rangle \end{aligned} \quad (+0.30)$$

$$|d^3\Sigma^+\rangle \approx 0.65 |1\sigma^2 2\sigma^2 (1\pi_x^2 2\pi_x^1 1\pi_y^2 + 1\pi_x^2 1\pi_y^2 2\pi_y^1)\rangle \quad (+0.06)$$

$$|e^3\Delta\rangle \approx 0.67 |1\sigma^2 2\sigma^2 (1\pi_x^2 2\pi_x^1 1\pi_y^2 - 1\pi_x^2 1\pi_y^2 2\pi_y^1)\rangle \quad (+0.05)$$

$$|D^1\Sigma^-\rangle \approx 0.64 |1\sigma^2 2\sigma^2 (1\pi_x^1 1\pi_y^2 2\pi_y^1 - 1\pi_x^2 2\pi_x^1 1\pi_y^1)\rangle \quad (+0.11)$$

$$\begin{aligned} |E^1\Delta\rangle &\approx 0.60 |1\sigma^2 2\sigma^2 (1\pi_x^2 2\pi_x^1 1\pi_y^1 + 1\pi_x^1 1\pi_y^2 2\pi_y^1)\rangle \\ &- 0.30 |1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1\rangle \end{aligned} \quad (+0.02)$$

$$|F^3\Sigma^-\rangle \approx 0.63 |1\sigma^2 2\sigma^2 (1\pi_x^1 1\pi_y^2 2\pi_y^1 + 1\pi_x^2 2\pi_x^1 1\pi_y^1)\rangle \quad (+0.01)$$

$$\begin{aligned} |F^1\Sigma^+\rangle &\approx 0.49 |1\sigma^2 2\sigma^2 3\sigma^2 (1\pi_x^2 + 1\pi_y^2)\rangle \\ &+ 0.36 |1\sigma^2 2\sigma^2 (1\pi_x^2 1\pi_y^1 2\pi_y^1 + 1\pi_x^1 2\pi_x^1 1\pi_y^2)\rangle \end{aligned} \quad (+0.06)$$

## 4. Synopsis and remarks

Complete potential energy curves of 18 electronic states of ZnS have been constructed at the MRCI/A5 $\zeta$  level of theory. For all bound states, we report total energies, dissociation energies, common spectroscopic constants, dipole moments, and energy separations at the MRCI/A5 $\zeta$  and MRCI + Q/A5 $\zeta$  levels. For three of the lowest states we performed, also, RCCSD(T) calculations which yielded similar to the MRCI + Q results. For the first four electronic states we included scalar relativistic corrections through the DKH method. These corrections led to bond shortenings of  $\sim 0.015$  Å and a slight decrease of the binding energies by 1–2 kcal/mol. These effects are expected to apply, also, to the rest of the excited states.

Three states, namely  $X^1\Sigma^+$ ,  $a^3\Pi$ ,  $A^1\Pi$ , were found to be bound with respect to the ground state atoms,  $Zn(^1S) + S(^3P)$ , by 34.8, 24.4, 18.7 kcal/mol, respectively, at the MRCI + DKH + Q/A5 $\zeta$  level. There is strong evidence that these states are non-adiabatically connected to the  $Zn(^3P) + S(^3P)$  excited asymptotic channel.

Finally, comparing our results with previous ZnO findings [30] the following remarks can be made: ZnO and ZnS have very similar PEC profiles with three low-lying states ( $X^1\Sigma^+$ ,  $a^3\Pi$ ,  $A^1\Pi$ ) closely spaced and bound with respect to the ground state atomic channel. ZnO has a more pronounced ionic character and, in general, larger binding energies. Both molecules have very large ground state dipole moments.

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