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K. Balasubramanian^{a)}

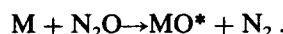
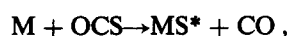
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Relativistic configuration interaction calculations of six ω - ω states [0^+ , 1 , 0^- (II), 0^+ (II), 0^+ (III)] and six λ - s states ($^1\Sigma^+$, $^3\Sigma^+$, $^3\Pi$, $^1\Pi$, $^3\Sigma^-$, and $^1\Sigma^-$) are carried out. These calculations enable assignment of the observed X , a , A , B , and C states. The nature of these states as well as other states which are yet to be observed is discussed. The properties of low-lying electronic states of PbS are compared with those of PbO. The dissociation energy of the ground state of PbS is calculated to be 3.83 eV.

I. INTRODUCTION

The electronic structure and spectroscopy of group (IV) chalcogenides is a topic of a number of investigations.¹⁻¹⁶ Many of the heavy group (IV) oxides and sulfides are generated in chemiluminescent reactions with high photon yields. A few of these reactions are shown below:



Since the above reactions are chemiluminescent, the suitability of these reactions as chemical laser pumping reactions have been investigated.

The first electronic spectrum of PbS was studied by Rochester and Howell.¹ These authors considered two absorption bands of PbS in the regions 2600–4500 and 3100–8000 Å. Vago and Barrow² later studied the UV absorption systems of PbS as well as PbO, PbSe, and PbTe. Barrow, Fry, and LeBargy³ studied four absorption systems of PbS which they assigned to $X \rightarrow a$, $X \rightarrow A$, $X \rightarrow B$, and $X \rightarrow D$ systems. Nixon and co-workers⁵⁻⁷ have studied the emission and vibronic spectra of PbS in inert gas and SF₆ matrices as well as the effect of neon matrix environment on the vibronic systems of PbS. Burtin *et al.*⁸ have studied the laser induced fluorescence spectra of PbS. Greenwood and Barrow⁹ have provided revised vibrational analysis of the a - X system as well as rotational analyses of bands of the C , C' - X systems. These authors have shown through their analyses that C and C' states are type c components of the $^3\Sigma^-$ state. Knockel *et al.*¹⁰ have carried out molecular beam studies of the X and A states of PbS. Using a molecular beam apparatus, these authors have recorded the laser excitation spectra and microwave-optical double-resonance spectra.

The dipole moment of the PbS molecule has been measured by microwave¹⁷ and Stark effect spectra.¹⁸ Thermodynamic studies of PbS and SnS using mass spectrometric techniques have revealed the binding energies for these systems.¹⁹ Through an analysis of experimental data, potential energy curves of some low-lying states of PbS have been constructed.²⁰ Some of these experimental works have been summarized by Huber and Herzberg.²¹

Relativistic *ab initio* calculations of PbO and SnO molecules have been carried out by Balasubramanian and Pitzer.^{13,14} These theoretical investigations shed light on the low-lying electronic states as well as electronic spectrum of these molecules. Further, theoretical investigation of heavy group (IV) chalcogenide ions was carried out by the present author²² with the intent of interpreting the photoelectron spectra of these molecules. Relativistic calculations of electronic properties of molecules containing very heavy atoms is a topic of considerable interest.²²⁻²³ This topic was reviewed by Pitzer,²³ Krauss and Stevens,²⁷ and more recently by Balasubramanian and Pitzer.³⁰

The above experimental and theoretical survey indicates significant interest on the electronic structure of PbS. The present theoretical investigation is undertaken with the objective of interpreting the electronic spectra of PbS as well as comparing the electronic properties of PbO and PbS. Section II describes the method of our investigation. Section III contains results and discussions which include comparison of the electronic states of PbS with PbO.

II. METHOD OF INVESTIGATION

The PbS molecule has a closed shell ground state [$X\ ^1\Sigma^+(0^+)$] arising from the $\sigma^2\pi^4$ electronic configuration, where we show only the valence p electrons. Table I shows a few low-lying electronic configurations of the PbS molecule, λ - s and ω - ω states arising from them. In that table the σ orbital is expected to be the bonding MO arising primarily from the interaction of S p_z with Pb p_z and s valence orbitals. The π orbital would be dominantly on S while the π^* orbitals would be dominantly on Pb, but slightly antibonding. Thus the spin-orbit splitting and contamination among the λ - s states with open shell excited configurations $\sigma\pi^4\pi^*$ and $\sigma^2\pi^3\pi^*$ would be very large. Table II shows the dissociation relationship of the few low-lying ω - ω electronic states of PbS. The energies of the dissociated atoms reported in that table were obtained from Moore's tables.³⁴

The atomic calculations of the lead atom were carried out by Balasubramanian and Pitzer in earlier papers on Pb₂ and Sn₂.^{32,33} As described in those papers, these calculations reproduced the atomic energy levels of the lead atom quite accurately.

The molecular orbitals of PbS were generated by a SCF calculation which employs a double- ζ Slater-type basis set

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TABLE I. A few MO configurations of PbS and the terms arising from them in λ - s and ω - ω coupling schemes.

Configuration	λ - S state	ω - ω state
$\sigma^2\pi^4$	$^1\Sigma^+$	0^+
$\sigma\pi^4\pi^*$	$^3\Pi$	$0^+, 0^-, 1, 2$
	$^1\Pi$	1
$\sigma^2\pi^3\pi^*$	$^3\Sigma^+$	$0^-, 1$
	$^3\Delta$	$1, 2, 3$
	$^3\Sigma^-$	$0^+, 1$
	$^1\Sigma^+$	0^+
	$^1\Delta$	2
	$^1\Sigma^-$	0^-

for the valence orbitals. We employ relativistic effective core potentials for Pb with the outer $d^{10}s^2p^2$ shell as the valence shell. We included all the electrons of the S atom in the SCF calculations. The SCF calculation of $\sigma^2\pi^4$ configuration does not produce a very good π^* orbital since this is a virtual orbital. Thus, states which arise from occupying the π^* orbital are not well described with the ground state SCF. Hence, we carried out SCF calculations for the $^3\Pi$ state which produce a reasonable π^* orbital. The CI calculations of excited states were carried out using this orbital.

Table III shows the STO basis set optimized for the ground state (3P) of the Pb and S atoms. As one can see from that table, the resulting basis set is double zeta in the valence space.

Configuration interaction calculations were carried out following SCF calculations. All λ - s states that give rise to states of the same ω - ω symmetry would mix in the relativistic configuration interaction calculations. Thus our calculations of the 0^+ state included $\sigma^2\pi^4$, $\sigma^2\pi^3\pi^*$, and $\sigma\pi^4\pi^*$ configurations as reference configurations. In order to introduce electron correlation and to describe the molecule well at long distances, we included the $\sigma^2\pi^2\pi^*\pi^*$, $\sigma^2\pi^*\pi^*$, $\sigma\sigma^*\pi^3\pi^*$ configurations as reference configurations. The 0^+ state thus included 19 Cartesian reference configurations and a total of 2480 configurations.

The 1 state calculations included $\sigma^2\pi^3\pi^*$ and $\sigma\pi^4\pi^*$ reference configurations with the spin and angular momentum chosen so as to yield a ω quantum number of 1. The 1 states included 8 reference configurations and a total of 1492 configurations. The 0^- states included 12 reference configurations and a total of 2137 configurations.

As described in the paper on PbO,¹³ since our calculations are based on Cartesian orbitals in C_{2v} symmetry, differ-

TABLE II. Molecular states of PbS and their dissociation limits.

Molecular states	Dissociation limit S + Pb	Atomic energies (cm ⁻¹)
$0^+, 1, 2$	$^3P_2 + ^3P_0$	0.0
$0^-, 1$	$^3P_1 + ^3P_0$	397
0^+	$^3P_0 + ^3P_0$	574
$0^+, 0^-(2), 1(3), 2(2), 3$	$^3P_2 + ^3P_1$	7819
$0^+(2), 0^-, 1(2), 2$	$^3P_1 + ^3P_1$	7978
$0^-, 1$	$^3P_0 + ^3P_1$	8204

TABLE III. Orbital exponents in Slater-type basis functions optimized for the 3P Pb and S atoms.^a

	Pb	S
s	1.9021 (4) 0.8482 (4)	15.7137 (1) 5.322 (2) 2.3515 (3) 1.911 (3)
p	1.5189 (4) 0.8599 (4)	6.282 (2) 3.7379 (4) 1.9512 (4)
d	3.5804 (4) 1.6047 (4)	

^a Numbers of parentheses are the principal quantum numbers.

ent $C_{\infty v}$ states involve the same Cartesian configurations with different sign relationships among coefficients. Thus our CI program could cause a collapse of a higher energy root of the desired symmetry to a lower root of another symmetry. For example, a 2 state, which has the same set of configurations as 0^- state, could collapse into an 0^- state. This collapse could, however, be avoided with fewer reference configurations, but the results are less accurate. The 0^+ (II) state calculations had all of the $^3\Pi(0^+)$, $^1\Sigma^+(0^+)$, and $^1\Sigma^+$ (II) (0^+) reference configurations. The 0^+ (III) state did not include $^3\Pi_{0^+}$ reference configurations.

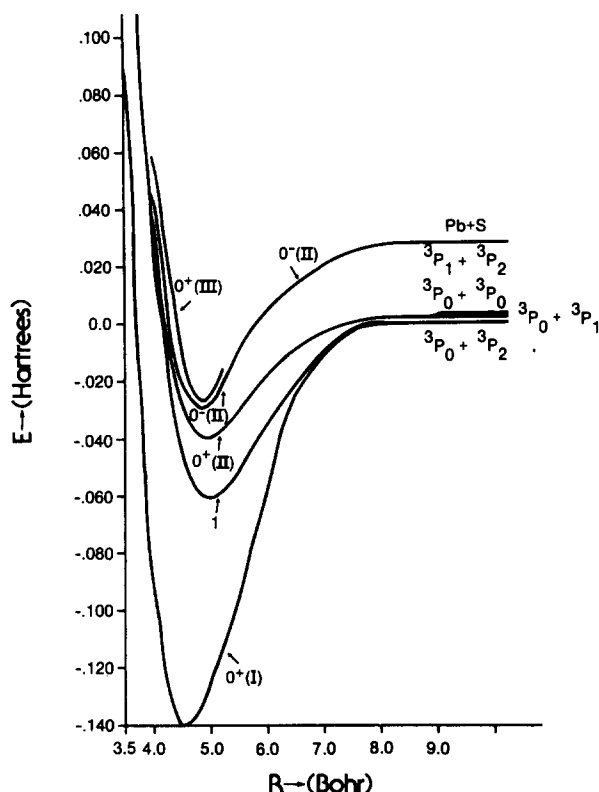
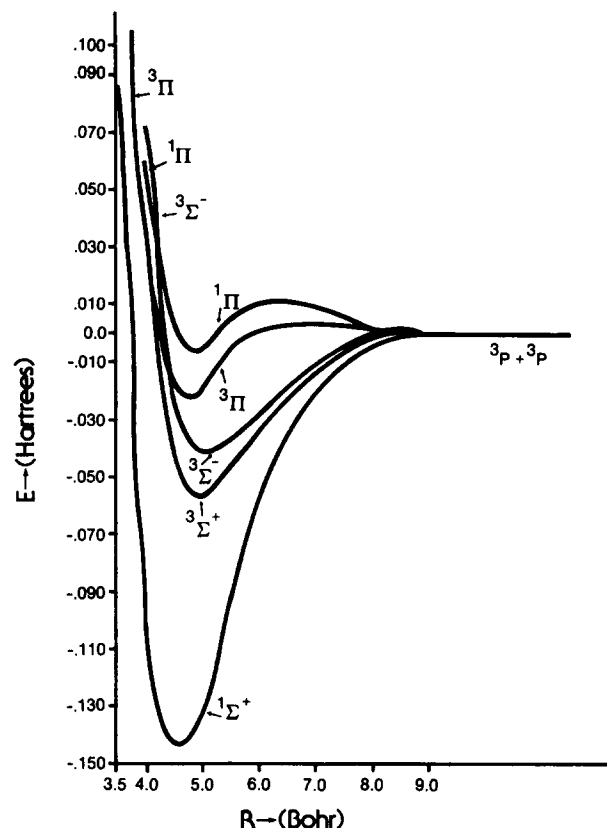
III. RESULTS AND DISCUSSIONS

Table IV shows the spectroscopic properties of PbS. Among the states listed in that table the X , a , A , and C states have been observed experimentally. We also report in Table IV the properties of a number of λ - s states calculated without spin-orbit interaction. Although these states were calculated without spin-orbit interaction, their properties are of immense use in assigning a number of experimentally observed transitions, since the PbS molecule is represented reasonably well in λ - s coupling.

The calculated potential energy curves of some of the ω - ω states are shown in Fig. 1. The potential energy curves

TABLE IV. Spectroscopic properties of PbS.

State	R_e Å		T_e (cm ⁻¹)		ω_e (cm ⁻¹)	
	Calc	Expt	Calc	Expt	Calc	Expt
$X\ 0^+(I)$	2.40	2.29	0.0	0.0	432	429
$a\ 1(I)$	2.63	2.56	17 533	14 893	321	286
$0^-(I)$	2.64	...	17 581	...	312	...
$A\ 0^+(II)$	2.61	2.51	22 256	18 853	282	261
$0^-(II)$	2.55	...	24 486	...	324	...
$C\ 0^+(III)$	2.60	...	24 698	23 213	395	304
$^1\Sigma^+$	2.40	...	1 645	...	446	...
$^3\Sigma^+$	2.62	...	20 691	...	332	...
$^3\Sigma^-$	2.68	...	24 144	...	295	...
$^3\Pi$	2.52	...	28 377	...	340	...
$^1\Pi$	2.57	...	31 611	...	327	...

FIG. 1. Potential energy curves of a few low-lying ω - ω states of PbS.FIG. 2. Potential energy curves of a few λ - s states of PbS.

of the λ - s states obtained without spin-orbit interaction are shown in Fig. 2.

The X ground state is of 0^+ symmetry and arises from the $\sigma^2\pi^4$ electronic configuration. The a state is the 1 component of $^3\Sigma^-$. The A state is the second root of 0^+ calculations. It is a mixture of $^3\Pi_{0^+}$ and $^3\Sigma_{0^-}$ with $^3\Pi_{0^+}$ making a dominant contribution. The C state is also of 0^+ symmetry and it corresponds to the third root of our 0^+ calculations.

The calculated vibrational frequencies of the electronic states of PbS are in remarkable agreement with the experimental values. The calculated R_e values are about 0.1 Å longer than the experimental values. This is attributed to basis set, correlation and errors introduced through the use of effective core potentials. For some of the excited states, the calculated T_e values are somewhat higher than the corresponding experimental values. This trend is attributed to the fact that in these calculations ground state is much better correlated than the excited states.

The electronic states of PbS exhibit a remarkable resemblance with the electronic states of PbO. The calculated T_e values exhibit a similar trend. The calculated R_e values for PbS are about 0.4 Å larger than the corresponding values for PbO. The ω_e values of PbS states are smaller than the ω_e values of PbO. It seems that based on the electronic properties of PbO, one could assign the electronic transitions observed in PbS. However, this may not be true of PbSe and PbTe, since spin-orbit contribution for Se and Te is much larger.

Unlike PbO, the 0^- states have not yet been observed for PbS. In Table IV, we have reported the properties of two 0^- states. Thus there is further room for study in the region of 15 000–25 000 cm^{-1} .

The calculated D_e value for the $X(0^+)$ state of PbS is 30 875 cm^{-1} or 3.83 eV. The experimental thermochemical value is about 3.49 eV. Thus our calculated D_e value is in very good agreement with the experimental value.

The ionization potential of PbS and other group (IV) chalcogenides were calculated earlier²² with the objective of interpreting the photoelectron spectra of SnO. The ionization potential of PbS calculated including spin-orbit interaction is 7.87 eV.

The highest occupied σ orbital is a mixture of Pb 6p and S 3p with S 3s also making a nonnegligible contribution. Thus there is strong σ bonding between Pb and S. The π orbital is dominantly on S but the lead p orbitals do make a small contribution. Consequently, there appears to be a weak π bonding also.

The $0^+(I)$ state is dominantly (85%) $^1\Sigma_0^+$ at the equilibrium geometry. The contribution of $^3\Pi_{0^+}$ is about 3%. The other states such as $(\sigma^2\pi^3\pi^*)_{0^+}$ and $(\sigma^2\pi^2\pi^{*2})_{0^+}$ account for about 3% of the population. The A $0^+[0^+(II)]$ state is a mixture of $^3\Pi_{0^+}$ and $^3\Sigma_{0^-}$ with $^3\Pi_{0^+}$ making dominant contributions at equilibrium distances. At very short distances it is predominantly $^3\Pi_{0^+}$ with small mixing with $^1\Sigma_0^+$. The $0^+(III)$ state is a mixture of $^3\Sigma_{0^-}$ and $^3\Pi_{0^+}$ with $^3\Sigma_{0^-}$ having the major component. The 1 state is a mixture of $^3\Sigma_1^+$ and $^3\Sigma_1^-$. The 0^- state is a mixture of $^3\Pi_{0^-}$, $^3\Sigma_0^+$, and $^1\Sigma_0^-$.

The avoided crossing of states arising from $\sigma^2\pi^3\pi^*$ configurations of a given ω - ω symmetry with a compatible $^3\Pi$ state of the same symmetry exhibited by PbO is also observed in PbS. The 1, 0^- , and $0^+(II)$ states are predomi-

nantly $^3\Pi_1$, $^3\Pi_0^-$, and $^3\Pi_0^+$ in the repulsive region of the potential curves. At near equilibrium distances these states are dominated by the corresponding $\omega-\omega$ states arising from the $\sigma^2\pi^3\pi^*$ configuration.

IV. CONCLUSION

In this investigation we carried out relativistic CI calculations of a number of low-lying electronic states of PbS. Calculations of the low-lying $\lambda-s$ states without spin-orbit interaction are also carried out. Our calculations confirm the earlier assignment of the experimentally observed X , a , A , and C states. The electronic states of PbS exhibit a remarkable resemblance with the corresponding states of PbO.

ACKNOWLEDGMENT

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