RELATIVISTIC CALCULATIONS OF ELECTRONIC STATES OF SnS

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Ab initio configuration interaction calculations which employ relativistic effective potentials for Sn are carried out for the X '\( \Sigma^+ \)\', '\( \Pi^+ \)\', '\( \Delta \)\', '\( \Sigma^- \)\', '\( \Pi \)\', and '\( \Sigma^+ \)\' (II) states of SnS. Spectroscopic properties of these states are computed and compared with available experimental results. The dissociation energy of SnS is calculated to be 4.2 eV. The nature of the observed electronic states as well as other electronic states yet to be observed is discussed.

1. Introduction

The electronic properties of heavy group IV oxides and sulfides have been of considerable interest [1–12] since they are potential candidates for chemical lasers. The following reactions which involve Sn and Pb atoms (M) are chemiluminescent:

\[ \text{M} + \text{OCS} \rightarrow \text{MS}^* + \text{CO}, \]
\[ \text{M} + \text{N}_2\text{O} \rightarrow \text{MO}^* + \text{N}_2, \]
\[ \text{M} + \text{O}_3 \rightarrow \text{MO}^* + \text{O}_2. \]

The electronic spectra of SnS [1–6], PbO [7], PbS [8,9] and SnO [10,11] have been investigated by a number of workers. The results of the earlier investigations on these molecules are summarized by Huber and Herzberg [12].

The absorption spectrum of SnS has been studied by a number of investigators [1–4]. The electronic transitions observed for SnS below 35000 cm\(^{-1}\) are designated as a \( \rightarrow \) X, A ↔ X, C' ↔ X, D ↔ X and E ↔ X.

Greenwood, Linton and Barrow [6] have studied the electronic spectrum of SnS using the chemiluminescence reaction listed above. Two electronic states excited in chemiluminescence have been characterized (a, \( \Lambda \)). These authors have assigned these to a '\( \Sigma^+ \)'(1) and A '\( \Pi \)'(0\(^+\)). These authors have also carried out extended rotational analysis of the perturbed bands observed in absorption which seem to enable tentative assignment for the \( \Omega \) component of '\( \Sigma^- \)' and '\( \Pi \)'(1). However, as noted by these authors, the observed spectrum is quite complex and the assignment of the many observed progressions into electronic band systems has proved to be difficult and remains uncertain. This is in part due to the existence of many low-lying electronic states for lead and Sn oxides and sulfides.

Ab initio calculations which include relativistic and correlation effects have been carried out on SnO [13], PbO [14] and PbS [15]. As noted by Greenwood, Linton and Barrow [6] the relative positions of the excited states of diatomic oxides and sulfides vary for various heavy atoms and thus a comparative study of the excited states of these systems could be valuable. Further, as noted in the above survey of experimental investigations on SnS, the assignments of observed bands remain difficult and uncertain. There are no theoretical calculations on SnS to date. The present investigation on SnS is undertaken with the objective of shedding light on the low-lying electronic states of SnS. We calculate the spectroscopic properties of a number of electronic states some of which have been observed while the others are yet to be observed. Electronic properties of molecules containing very heavy atoms is a topic actively being investigated by many workers (see refs. [17–20] for a review of this topic).
Table 1

Molecular states of SnS and their dissociation limits

<table>
<thead>
<tr>
<th>Molecular state</th>
<th>Dissociation limit</th>
<th>Atomic energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0⁺,1,2</td>
<td>3P₀⁺-3P₂</td>
<td>0.0</td>
</tr>
<tr>
<td>0⁻,1</td>
<td>3P₀⁻-3P₁</td>
<td>397</td>
</tr>
<tr>
<td>0⁺</td>
<td>3Pₐ⁺-3P₀</td>
<td>574</td>
</tr>
<tr>
<td>0⁺,0⁻(2),1(3),2(2)</td>
<td>3P₁⁺,3P₂</td>
<td>1692</td>
</tr>
<tr>
<td>0⁺(2),0⁻-1(2),2</td>
<td>3P₁⁺-3P₁</td>
<td>2089</td>
</tr>
</tbody>
</table>

2. Method of investigation

In earlier investigations on PbS [15] and SnO [13] the low-lying electronic states in both λ-σ and ω-ω coupling schemes have been enumerated. The ground state of the SnS molecule is expected to be the 1Σ⁺ state arising from the σ²π₄ configuration where we show only the outer p electrons on Sn and S. Table 1 shows the dissociation relationship for the low-lying electronic states of SnS. As one can see from that table, there are many electronic states which dissociate into atomic states with energy less than 2100 cm⁻¹.

We employ relativistic effective core potentials with the outer 4d¹⁰s⁵p² shell of the tin atom explicitly retained in the valence space. A Slater-type basis set for the tin atom employed earlier by Balasubramanian and Pitzer [13] for SnO is used in the present calculations. An all-electron STO basis for the S atom optimized for the 3P ground state used earlier for PbS [15] is employed here. As noted by Balasubramanian and Pitzer [13] it was necessary to optimize the π* orbital which is unoccupied in the 1Σ⁺ ground state of SnO since this orbital is poorly described for the excited states. Thus two sets of SCF calculations were carried out one for the 1Σ⁺ state and the other for the 3Π state arising from the σ⁴π* configuration which has an occupied π* orbital.

Configuration interaction calculations were carried out following the SCF calculations. In general, it would be necessary to carry out relativistic CI calculations since λ-σ states of different symmetry could mix in the presence of spin–orbit interaction. However, Balasubramanian and Pitzer [13] have noted that the effect of spin–orbit terms on the energies and spectroscopic properties are somewhat small for SnO and one could assign the observed electronic bands without spin–orbit terms. Since the addition of spin–orbit terms increases the configuration space substantially, it was decided to carry out CI calculations without spin–orbit terms. Since the spin–orbit splitting (3P₁⁻3P₀) for S is 574 cm⁻¹, in comparison to the corresponding value for O (385 cm⁻¹) [21], we believe that the present calculations on SnS are comparable in accuracy to the earlier calculations on SnO [13]. Since we employ a CI space similar to the one for SnO, we only mention that the present RCI calculations includes single and double excitations from a multireference configuration list. It is, however, noted that the 1Σ⁺ ground state is treated at a more accurate level than the excited states, since attempts were made to calculate the dissociation energies of the ground state as accurately as possible. Thus, the excited states are about 15% higher in energy in comparison to the ground state. Since all excited states are off by about the same percentage, we could estimate the actual separations within reasonable accuracy. The CI calculations were carried out using a modified version of the code developed based on ref. [22].

3. Results and discussion

The calculated spectroscopic properties of the electronic states of SnS are shown in table 2. These properties were calculated without spin–orbit interaction. However, as noted in section 2, the spin–orbit interaction would change the Tₐ value by almost 5–6%. The Rₐ and ωₐ values would be influenced to a smaller extent by the spin–orbit term. The potential energy curves of some of the calculated states are shown in fig. 1.

The lowest excited electronic state of SnS is 3Σ⁺ and has been observed by Greenwood, Linton and Barrow [6] in chemiluminescence. As noted in section 2, the Tₐ values of all the excited states are about 15% higher than the true values since the ground state was correlated more than the excited states. If one applies this correction to all the excited states, the observed values are in reasonable agreement with our calculated results. Our calculations thus confirm the tentative assignment of the a state to the 3Σ⁺(1) component since there is no other electronic state in...
Table 2
Spectroscopic properties of SnS

<table>
<thead>
<tr>
<th>State</th>
<th>( R_e (\text{\AA}) )</th>
<th>( T_e (\text{cm}^{-1}) )</th>
<th>( \omega_e (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc.</td>
<td>exp.</td>
<td>calc.</td>
</tr>
<tr>
<td>( \text{C'\Sigma}^+ )</td>
<td>2.32</td>
<td>2.21</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{a3\Sigma}^+ (0^-,1) )</td>
<td>2.55</td>
<td>–</td>
<td>21864</td>
</tr>
<tr>
<td>( \text{3\Sigma}^- (0^-,1) )</td>
<td>2.62</td>
<td>–</td>
<td>25632</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{3\Delta}(3,2,1) )</td>
<td>–</td>
<td>–</td>
<td>( \approx 24000 )</td>
</tr>
<tr>
<td>( \text{3\Sigma}^- (0^-) )</td>
<td>2.62</td>
<td>–</td>
<td>25685</td>
</tr>
<tr>
<td>( \text{B'\Pi} )</td>
<td>2.42</td>
<td>–</td>
<td>28658</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{D'\Pi} )</td>
<td>2.48</td>
<td>2.36</td>
<td>32707</td>
</tr>
<tr>
<td>( \text{E'\Sigma}^+ (\Pi) )</td>
<td>2.63</td>
<td>–</td>
<td>41238</td>
</tr>
</tbody>
</table>

This region and a transition to \( \text{3\Sigma}^+ (0^-) \) is not allowed from the ground state.

Above the \( \text{3\Sigma}^+ \) state we found a \( \text{3\Delta} \) electronic state. Since transition to this state is forbidden in both \( \lambda-\delta \) and \( \omega-\omega \) coupling from the ground state, this state cannot be easily observed experimentally. Although we did not calculate the properties of this state at all internuclear distances, the \( T_e \) value at the present level of calculations was found to be \( 24000 \text{ cm}^{-1} \). Correcting for the differential correlation errors, we predict that the \( T_e \) value of this state should be about \( 20400 \text{ cm}^{-1} \) in the absence of spin–orbit interaction.

Greenwood, Linton and Barrow [6] have observed the spectrum of SnS excited in chemiluminescence. These authors observed five systems for which the rotational analyses have been carried out [6]. Based on the fact that the transitions of system 5 and system 4 have three-branch bands, these authors could assign the upper states of systems 4 and 5 to \( \Omega=1 \) components. The systems 2 and 3 were assigned to \( \Omega=0^+ \). The first system with an experimental \( T_e \) value of \( 18144 \text{ cm}^{-1} \) was assigned to \( \text{3\Sigma}^+ (1) \) which we discussed earlier. Greenwood, Linton and Barrow [6] assign the bands in systems 2–5 based on a comparison to the ordering of lead compounds for which

\[ \text{C'\Omega}(1)(3\Sigma^-) > \text{C\Omega}0^+(3\Sigma^-) > \text{B\Omega}(3\Pi) > \text{A\Omega}0^+(3\Pi) > \text{a1}(3\Sigma^+) > \chi'\Sigma^+. \]

The earlier theoretical calculations on PbO [14] and PbS [15] support the above ordering. Further, these authors argue that the spin–orbit splitting for the \( \text{3\Pi}_{0^-}-\text{3\Pi}_1 \) states is larger than the \( \text{3\Sigma}^+_{0^-}-\text{3\Sigma}^-_1 \) splitting for SnS. Based on these arguments, Greenwood, Linton and Barrow [6] assign system 5 (\( T_e = 23320 \))
cm$^{-1}$) to the B$^3\Pi_1-X^1\Sigma^+$ system, system 4 ($T_e=22480$ cm$^{-1}$) to the C$^2\Sigma^+_1-X^1\Sigma^+$ system, system 3 ($T_e=22390$ cm$^{-1}$) to C$^3\Sigma^0_0-^1\Sigma^+$, and system 2 ($T_e=22021$ cm$^{-1}$) to the A$^3\Pi_0-^1\Sigma^+$ system. As one can see from table 2 when one corrects for the differential correlation errors the $T_e$ value of the $3\Sigma^-$ state falls very close to the $T_e$ values of the C and C' states. The calculated $^3\Pi$ energies are somewhat higher but similar to the energies of the $^3\Sigma^-$ state. The $^3\Pi$ state arises from the $\sigma^3\pi^3\pi^*$ configurations while the $^3\Sigma^-$ state arises from $\sigma^2\pi^3\pi^*$ configurations. Since the spin–orbit splitting is determined primarily (to first order) by the nature of the open-shell orbitals, it was decided to investigate the $\sigma$, $\pi$ and $\pi^*$ orbitals. The contribution of the tin atom is significant for the $\sigma$ and $\pi^*$ orbitals, while the $\pi$ orbital is dominantly a $S\,p$ orbital with the $\pi$ making only a small contribution. Thus the $\sigma^3\pi^3\pi^*$ configurations involve two open-shell orbitals ($\sigma,\pi^*$) for which the tin atom makes significant contribution while the $\sigma^2\pi^3\pi^*$ involves only one open-shell orbital ($\pi^*$) for which the tin atom makes substantial contribution. Since the spin–orbit splitting of SnS would depend mainly on the contribution of the tin atom to the open-shell molecular orbitals, the spin–orbit splitting of $^3\Pi$ would be larger (since for both the open shells Sn contribution is significant) than $^3\Sigma^-$ (since only the $\pi^*$ orbital is predominantly Sn).

Although the above arguments support the assignment C$^3\Sigma^0_0$, C$^3\Sigma^+_1$, B$^3\Pi_1$ and A$^3\Pi_0$, it must be pointed out that the experimental C$^3\Sigma^0_0-^3\Sigma^+_1$ splitting of 100 cm$^{-1}$ is somewhat small. The corresponding splittings for PbO [14] and PbS [15] are 1127 and 1811 cm$^{-1}$, respectively. For SnO, it appears that the C' state has not been observed. Thus, the C–C' splitting of SnO could not be compared with SnS. However, the A–B ($^3\Pi_0,^3\Pi_1$) splitting of PbO and PbS are 2422 and 2996 cm$^{-1}$, respectively. The corresponding splitting for SnO (557 cm$^{-1}$) suggests that if the assignments by Greenwood, Linton and Barrow [6] are correct then the A–B splitting of SnS should be approximately 570 cm$^{-1}$ larger than the corresponding splitting for SnO. The A–B splitting calculated this way, about 1130 cm$^{-1}$, is not very far from the 1299 cm$^{-1}$ obtained by Greenwood, Linton and Barrow [6]. For a conclusive assignment of the observed A, B, C and C' states, the experimental $R_e$ values are needed for these states. As one can see from table 2, the calculated $R_e$ value of the $^3\Pi$ state is considerably shorter than the $R_e$ value of the $^3\Sigma^-$ state. Thus, experimental $R_e$ values should be obtained for these states.

The vibrational frequencies of the A, B, C and C' states could not be calculated accurately from experimental results [6]. As Greenwood, Linton and Barrow [6] note the observed bands are perturbed. Further, the A($0^+$) and C($0^+$) states are only 380 cm$^{-1}$ apart implying that mixing between $^3\Sigma^0_0$ and $^3\Pi_0$ could be large. Thus, the $\omega_e$ values of these states could be influenced by this mixing. For the A state, however, a reliable experimental $\omega_e$ could be obtained and agrees well with the theoretical value as one can see from table 2. Thus, the theoretical $\omega_e$ values for other electronic states listed in table 2 could be valuable in further analysis of observed bands.

The $R_e$ and $\omega_e$ values of the D$^1\Pi$ state are in reasonable agreement with the experimental values but the calculated $T_e$ value of this state is a bit higher. This trend is consistent with analogous calculations on PbS in the absence of spin–orbit interaction for which the $^1\Pi$ state is 31611 cm$^{-1}$ above the ground state. The $\omega_e$ value of the E state follows the experimental trend. The E state is treated at a somewhat lower level theoretically. Further, since this is quite excited, calculations of energies were difficult and could be sensitive to basis set.

The calculated dissociation energy of the $^1\Sigma^+$ in the absence of spin–orbit interaction is 4.48 eV. The spin–orbit contribution to the closed shell ground state would, of course, be zero. However, in the dissociation limit, the $^3\Pi_0$ state of the Sn atom is lowered by 0.33 eV [23] in comparison to the $^3\Pi$ state by spin–orbit interaction. Thus, the calculated $D_e$ value in the absence of spin–orbit interaction should be lowered by 0.33 eV which yields 4.15 eV. This value is in very good agreement with the thermochemical value of 4.77 eV [12]. The approximate $D_d^G$ ($\leqslant$4.84 eV) [12] derived from the continuous absorption (assuming dissociation into $^1D+^1D$) is thus not unreasonable.

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The nature of low-lying electronic states and the orbitals are discussed next. If one includes only the outer s and p shells of Sn and S, the ground state of SnS is predominantly $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$. At the equilibrium geometry of the ground state, the 1$\sigma$ orbital is predominantly sulfur 3s orbital with small contribution from Sn s and d. The 2$\sigma$ orbital is predominantly Sn s but sulfur 3s makes non-negligible contribution and is slightly antibonding. The 3$\sigma$ orbital is the bonding MO resulting from Sn s, p and S 3p. The 1$\pi$ orbital is mainly on S with Sn p making small contribution. The 1$\pi^*$ orbital is the antibonding combination of Sn and S p orbitals but the Sn orbital makes a greater contribution. The $1\pi^*$ state is 89% $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ and 2% $1\Sigma^+ (1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\pi^*)$ at the near equilibrium geometries. The $3\Pi$ and $1\Pi$ states are predominantly $1\sigma^2 2\sigma^2 3\sigma 1\pi^4 1\pi^*$. The $3\Sigma^-$, $3\Sigma^+$, $1\Delta$, $1\Sigma^-$ states are predominantly $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\pi^*$. The $1\Sigma^+$ (II) state (E) is 42% $1\Sigma^+ (1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\pi^*)$, 31% $(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\pi^*)$ and 13% $1\Sigma^+ (1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4)$. Thus the E ($1\Sigma^+ (II)$) state is somewhat more complex than other electronic states.

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References