Spectroscopic Properties of SbH

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Relativistic configuration interaction calculations which include spin–orbit interaction are carried out for nine low-lying $\omega$-$\omega$ states and four $\lambda$-$\lambda$ states. Spectroscopic properties of six bound $\omega$-$\omega$ states are reported. These calculations not only enable assignment of the experimentally observed $X_1, X_2, A_1, A_2,$ and $B$ states but also predict the properties of other electronic states ($0^+(II), 0^+(IV), 2, 2(II), 1(II), 0^-$) which are yet to be observed. The dissociation energy of SbH is predicted to be $2.7 \pm 0.2$ eV. © 1987 Academic Press, Inc.

1. INTRODUCTION

The SbH radical has been observed in the flash photolysis of stibine (SbH₃) by a few authors (1–3). Bollmark and Lindgren (1) have studied the absorption spectra of the SbH radical in the region 3300–3450 Å. These authors have assigned the observed bands in this region due to $3\Pi-3\Sigma^-$ systems by a comparison with the electronic spectra of isoelectronic NH and PH. From the rotational constant of the ground state, these authors have calculated the bond length of the ground state to be 1.7 Å.

Basco and Yee (2) have also studied the $3\Pi-3\Sigma^-$ system. These authors note that only the $3\Pi_0^+ - 3\Sigma^-$ system has rotational structure. The other bands of this system were found to be diffuse. Bollmark and Lindgren (3) have carried out the rotational analysis of the absorption spectra of SbH observed earlier. From this analysis these authors infer that the spin–orbit splitting of the ground state ($0^+ - 1$ splitting) is 660 cm⁻¹. The $3\Pi$ state was found to be predissociated. The existence of $B0^+$ and $C0^+$ states which cause perturbation to the $3\Pi_0^+$ bands was also inferred by these authors (3). The electronic spectra of isoelectronic AsH as well as BiH are also of considerable interest (4–6).

In earlier investigations (7, 8), one of the present authors (K.B.) studied the spectroscopic properties and potential energy curves of several electronic states of BiH. The electronic structure of isoelectronic BiF was also studied (9). These investigations have revealed several fascinating facts on the properties of electronic states of these molecules such as avoided crossings. Further, the spin–orbit interaction was found to have significant effect on the properties of electronic states of these molecules. For

1 Alfred P. Sloan fellow; Camille and Henry Dreyfus Teacher-scholar.
example, the excited states of BiH show significant spin–orbit mixings which vary as a function of internuclear distance leading to barriers and steps in the potential energy curves of these molecules.

Theoretical studies of spectroscopic properties of molecules containing very heavy atoms are quite challenging since such molecules contain a very large number of electrons and exhibit relativistic effects. Stimulated by both theoretical and experimental interest on heavy group (V) hydrides, we decided to extend the earlier investigation on BiH to SbH. We employ a relativistic configuration interaction technique described elsewhere (10). The relativistic CI treatment for BiH described in Ref. (8) is employed here for SbH. Section 2 briefly discusses the method of investigation while Section 3 outlines and discusses the results.

2. METHOD OF INVESTIGATION

The general methods of relativistic quantum chemistry have been recently reviewed by Balasubramanian and Pitzer (11). The readers are referred to that article for general details. We employ a double-zeta Slater-type basis for the antimony atom optimized for the 4S ground state. This basis set is shown in Table I. The hydrogen basis set is the same as the one employed by Balasubramanian (7, 8) in his BiH investigations.

The enumeration of low-lying electronic states, their dissociation limits, as well as the choice of reference configurations for the relativistic CI, were discussed by Balasubramanian (7, 8) in considerable detail in his BiH papers. Readers are referred to these references for details. In this investigation we employ the same relativistic CI as the one employed in Ref. (8) for BiH.

3. RESULTS AND DISCUSSION

Table II shows the spectroscopic properties of the low-lying electronic states of SbH. Among the states considered here, the 0+, 1, 2, 0+(II), 0+(III), 0+(IV), as well as the

<p>| TABLE I |</p>
<table>
<thead>
<tr>
<th>Slater-Type Basis Set for the Sb Atom (Numbers in Parentheses are Principal Quantum Numbers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
</tr>
<tr>
<td>s</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>p</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>d</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
TABLE II
Spectroscopic Properties of SbH

<table>
<thead>
<tr>
<th>State</th>
<th>$R_e$ (Å)</th>
<th>$T_e$ (cm$^{-1}$)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^+(1)$</td>
<td>1.81</td>
<td>1.72</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1.81</td>
<td>--</td>
<td>696</td>
</tr>
<tr>
<td>2</td>
<td>1.81</td>
<td>--</td>
<td>9 362</td>
</tr>
<tr>
<td>$0^+(I)$</td>
<td>1.80</td>
<td>--</td>
<td>15 772</td>
</tr>
<tr>
<td>$0^+(III)$</td>
<td>1.87</td>
<td>--</td>
<td>30 788</td>
</tr>
<tr>
<td>$0^+(IV)$</td>
<td>--</td>
<td>--</td>
<td>34 891</td>
</tr>
<tr>
<td>$3\Sigma^-$</td>
<td>1.81</td>
<td>--</td>
<td>919</td>
</tr>
<tr>
<td>$1\Delta$</td>
<td>1.81</td>
<td>--</td>
<td>9 607</td>
</tr>
<tr>
<td>$1\Sigma^+$</td>
<td>1.79</td>
<td>--</td>
<td>17 876</td>
</tr>
</tbody>
</table>

$3\Sigma^-$, $1\Delta$, $1\Sigma^+$ λ–σ states, are found to be bound. The potential energy curves of the low-lying $\omega$–ω states are shown in Fig. 1. Figure 2 shows the potential energy curves of $3\Sigma^-$, $1\Delta$, $1\Sigma^+$, and $5\Sigma^-$ λ–σ states of SbH obtained without spin–orbit interaction.

The $A^3\Sigma^+$ system observed in absorption is assigned to the $0^+(III)$ ($^3\Pi_0^+\leftarrow X(0^+)$ transition). The calculated and observed $T_e$ values are in very good agreement. As we can see from Table II, there are no experimental $\omega_e$ values available for the electronic states of SbH. Vibrational analysis of the observed bands is thus desirable to compare our calculated $\omega_e$ values.

The spin–orbit splitting ($0^+–1$ splitting) of the ground state is calculated to be 696 cm$^{-1}$. This value is in very good agreement with the value of 660 cm$^{-1}$ obtained by Bollmark and Lindgren (3) from the rotational analysis.

As one can see from Table II, our calculations predict the spectroscopic properties of a number of states (1, 2, $0^+(II)$, $0^+(IV)$) which are yet to be observed. The $0^+(II)$–$0^+(I)$ system corresponds to $1\Sigma^+_0^+–3\Sigma^+_0^+$ transition. The interaction between $3\Sigma^+_0^+$ and $1\Sigma^+_0^+$ is found to be nonnegligible due to spin–orbit interaction for SbH. Thus, this transition should be observable. Our calculations predict this transition to be observable in the region of 15 770 cm$^{-1}$. The analogous transition for BiH ($A^1\Pi^–X^0^+$) is observed in the 21 263-cm$^{-1}$ region (5).

The $0^+(IV)$–$X^0^+$ transition should be observable in the 35 000-cm$^{-1}$ region. Bollmark and Lindgren (3) have observed a C state which perturbs the bands of the $A^3\Pi_0^+–X^0^+$ system. The $T_0$ value of the C state is about 30 566 cm$^{-1}$.

The calculated dissociation energy of the SbH radical is 2.26 eV. There is no experimental $D_e$ value for the SbH radical. Since our calculations yield about 85% of the experimental $D_e$ value due to neglect of higher-order correlation corrections and a somewhat small basis set, we predict that the $D_e$ of SbH is about 2.7 ± 0.2 eV.

Figure 1 shows a number of repulsive curves for SbH. Specifically, the $0^–$, 2(II)
(shallow), and 1(II) states are $^3\Pi_0^-$, $^3\Pi_2$, and $^3\Pi_1$ components dominantly at short distances. The diffuse bands observed in the SbH absorption spectra could thus be attributed to the $^3\Pi_1-X^3\Sigma_0^+$ and $^3\Pi_2-X^3\Sigma_0^+$ systems. The calculated splittings of these states are in reasonable agreement with the regions where these bands are observed (2, 3).

The ground state $X_1(0^+)$ of SbH was found to be 92% $^3\Sigma_0^-$ arising from the $\sigma^2\pi^2$ configuration and 3% $^1\Sigma_0^+$ at its equilibrium geometry. The 0+(II) state was found to be 88% $^1\Sigma_0^+$ and 4% $^3\Sigma_0^+$. The 1(I) and 2 states are dominantly $^3\Sigma_1^+$ and $^1\Delta_2$ (95%), respectively, at near-equilibrium geometries. The 0+(III) state is 90% $^3\Pi_0^+$ at its equilibrium geometry, while the 0+(IV) state is a mixture of $^3\Pi_0^+ (\sigma^2\sigma^*\pi^2)$, $^1\Sigma_0^+ (\sigma^2\pi^2)$, and $^3\Pi_0^+ (\sigma\pi^2)$.

The electronic states of SbH exhibit avoided crossings analogous to BiH which were discussed in earlier investigations (7, 8). Specifically, the barrier in the 2 curve is due
Fig. 2. Potential energy curves of low-lying states of SbH in the absence of spin–orbit interaction.

to the avoided crossing of $^1\Delta_2$ with $^5\Sigma_2^-$. Similarly, the $^0\Sigma^-$ state becomes dominantly $^5\Sigma_0^-$ at long distances. The $0^+(III)$ and $0^+(IV)$ states of SbH were found to be similar to the corresponding states of BiH whose properties as a function of internuclear distance have been discussed in considerable detail in earlier investigations (7, 8), although the spin–orbit contamination is found to be smaller for SbH.

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Fig. 1. Potential energy curves of low-lying electronic states of SbH including spin–orbit interaction.

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