THE PREDICTED SPECTRUM OF THE SbH$_2$ MOLECULE IN ITS LOWEST TWO RENNER-DEGENERATE...
An *ab initio* study of the Renner effect and spin-orbit coupling in SbH₂ and BiH₂

Bojana Ostojić, a Peter Jensen, b Peter Schwerdtfeger, c and Philip R. Bunker d

aUniversity of Belgrade, Serbia; bBergische Universität Wuppertal, Germany; cMassey University Auckland, New Zealand; dSteacie Laboratory, National Research Council of Canada, Ottawa, Ontario, Canada.

Introduction

We present the results of *ab initio* calculations for the two lowest electronic states of the Group 15 dihydrogenides, SbH₂ and BiH₂. For each of these molecules the two lowest electronic states, \( \Sigma^1 \) and \( \Pi^1 \), become degenerate at linearity as a \( \Sigma^1 \) state and are therefore subject to the Renner effect (Fig. 1). Spin-orbit coupling is also strong in these two heavy-element containing molecules. We construct the three-dimensional potential energy surfaces and corresponding dipole moment and transition moment surfaces by multi-reference configuration interaction techniques involving these two electronic states for SbH₂. Including both the Renner effect and spin-orbit coupling, we calculate binding potential curves and the spin-orbit coupling constant for comparison.

Table 1: Calculated rovibronic term values (in cm⁻¹) for selected \( \nu_1, \nu_2, \nu_3 \) states of SbH₂ (SbH₂).

<table>
<thead>
<tr>
<th>Term Value</th>
<th>( \nu_1, \nu_2, \nu_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>1532.111</td>
</tr>
<tr>
<td>(1,0,0)</td>
<td>1337.604</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>1341.803</td>
</tr>
<tr>
<td>(0,1,0)</td>
<td>1433.737</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>1350.006</td>
</tr>
<tr>
<td>(0,2,0)</td>
<td>1361.105</td>
</tr>
</tbody>
</table>

Calculations

We have computed energies on the potential energy surfaces of the \( \Sigma^1 \) and \( \Pi^1 \) electronic states of SbH₂ and BiH₂ with the MOLPRO 2010.1 program packages [1], employing an all-electron CASSCF method, followed by an MCRI treatment. For hydrogen we used a aug-cc-pV2Z basis set, for antimony a Sapporo-KRDK-ζQZ-2012 basis set, and for bismuth a segmented all-electron contracted ESP basis set constructed for use with the non-relativistic DHK Hamiltonian.

Term Values for SbH₂

Thus far, we have carried out calculations of rovibronic term values for \( \Sigma^1 \) and \( \Pi^1 \) states of SbH₂ and BiH₂, by means of the REISSER program system [2]. Values for \( \Sigma^1 \)SbH₂, \( \Pi^1 \)SbH₂, \( \Sigma^1 \)BiH₂, \( \Pi^1 \)BiH₂, \( \Sigma^2 \)SbH₂, and \( \Sigma^2 \)BiH₂ are available, but we list only those for \( \Sigma^1 \)SbH₂ here. Simulations of rovibronic spectra are under way.

Local Mode Vibrations and Energy Clusters

We focus on the vibrational pattern of the SbH₂ molecule and the groundstate energy patterns are explained in terms of the Harmonically-Coupled-Anharmonic-Oscillator (HCAO) model (see Refs. [5, 6] and references therein), which maps a Hamiltonian representation matrix for a given state \( |n\rangle \) of the Morse oscillator basis functions \( |\nu_{11}\rangle \) with \( \nu_{11} = n \). The energy patterns depend on three parameters \( \alpha_1, \beta_1, \) and \( \Lambda_1 \). Types of \( \nu_{11} \), \( \nu_{12} \), and \( \nu_{22} \) are illustrated in Fig. 2. In reality, the characteristic patterns are sometimes ‘spoiled’ by interactions with nearby \( \nu_{11}, \nu_{12}, \nu_{22}, \nu_{33} \) states having \( \nu_{11} \approx 0 \), these states are not accounted for by the HCAO model.

![Figure 3: Rotationally degenerate level diagram for the vibrational ground state (left) and the \( \nu_{11}, \nu_{12}, \nu_{22} \) states (right) of SbH₂. The energies are plotted relative to the highest energy in each manifold. The term values are colour-coded according to the scheme to illustrate the \( \nu_{11}, \nu_{12}, \nu_{22} \) state transitions to the molecular symmetry group (9, \( \nu_{11} \), \( \nu_{12} \), \( \nu_{22} \), \( \nu_{33} \)).](image)

The vibrational energy level clusters caused by local-mode effects are accounted for by rovibronic energy clusters at high rotational excitation [5, 6]. Values are analogous to the ones formed in the \( \Sigma^1 \) and \( \Pi^1 \) electronic states of the \( \text{PH}_2 \) radical [8]. Figure 3 shows examples of this; they are term value diagrams for the vibrational ground state (left), and the \( \nu_{11}, \nu_{12}, \nu_{22} \) states (right), of \( \Sigma^1 \)SbH₂ electronic states of the \( \text{PH}_2 \) radical [8]. In both displays, we recognize the formation of four-fold energy clusters, the states in each cluster being symmetry \( \Delta \text{EC} + \Delta \text{EC} = \Delta \text{EC} \) [11] in the molecular symmetry group [9, 10]. The energy clusters in Fig. 3(left) are of Type II [12]; they include only one vibrational state, the vibrational ground state \( \Sigma^1 \)SbH₂. The energy clusters in Fig. 3(right) are formed by coalescence (increasing \( \nu_{11} \)) of two energy doublets, one doubling belong to the \( \nu_{22} \) vibrational state and the other one to the \( \nu_{12} \) vibrational state. Such clusters are of Type II [12].

Conclusions

In the matrix isolation infrared (IR) and Raman spectra, only pure \( \Sigma^1 \) states were detected, with hydrogen containing, under normal Raman conditions in different environments: pure \( \text{Ne}_2 \), \( \text{Ar}_2 \), \( \text{Ne}_2 \), \( \text{Ar}_2 \), and \( \text{Ar}_2 \). In each environment, two bands were identified as the stretching vibrational fundamentals of \( \text{SbH}_2 \), \( \text{SbD}_2 \), or \( \text{SMD} \). In the table, we have summarized the experimental results and compared them to our predicted fundamental wavenumbers, which obviously support the assignments. A spectrum attributed to the absorption spectrum of \( \text{SbH}_2 \) \( \lambda \) was obtained in Ref. [14] by the flash photolysis of tellurium (SMEH). Also, in Ref. [15] the emission spectrum of \( \text{SbH}_2 \) \( \lambda \) (400–700 nm) was recorded with a resolution of 12Å, and a portion of the spectrum from 485 to 535 nm was recorded with a resolution of 3 Å. We intend to compare our spectral simulations, which are currently being calculated, with these experimental spectra to confirm or refute the assignments.

References


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