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# An *ab initio* study of the Renner effect and spin-orbit coupling in SbH<sub>2</sub> and BiH<sub>2</sub> **Bojana Ostojić**,<sup>*a*</sup> **Per Jensen**,<sup>*b*</sup> **Peter Schwerdtfeger**,<sup>*c*</sup> **and Philip R. Bunker**<sup>*d*</sup>

<sup>a</sup>University of Belgrade, Serbia; <sup>b</sup>Bergische Universität Wuppertal, Germany; <sup>c</sup>Massey University Auckland, New Zealand; <sup>d</sup>Steacie 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 (pnictogen) dihydrides, SbH<sub>2</sub> and BiH<sub>2</sub>. For each of these molecules the two lowest electronic states,  $X^2B_1$  and  $\tilde{A}^2 A_1$ , become degenerate at linearity as a  $1^2 \Pi_u$  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 SbH<sub>2</sub>. Including both the Renner effect and spin-orbit coupling, we calculate rovibronic term values for SbH<sub>2</sub>. For the heavier dihydride BiH<sub>2</sub> we calculate bending potential curves and the spin-orbit coupling constant for comparison.



**Figure 1:** The bending potential energy functions of SbH<sub>2</sub> in the  $\tilde{X}^2B_1$  and  $\tilde{A}^2A_1$ electronic states. The bond lengths are both held fixed at the value  $r^{(\text{ref})} = 1.719$  Å. The energies of the lowest bending eigenstates with  $K_a = 0$  are indicated for the two electronic states.  $\rho = 180^{\circ} - \angle (H-Sb-H)$ .

### Ab initio Calculations

We have computed energies on the potential energy surfaces of the  $\tilde{X}^2 B_1$  and  $\tilde{A}^2 A_1$  electronic states of SbH<sub>2</sub> and BiH<sub>2</sub> with the MOL-PRO 2010.1 program package [1], employing an all-electron CASSCF method, followed by a MRCI treatment. For hydrogen we used a augcc-pV5Z basis set, for antimony a Sapporo-DKH3-QZP-2012 basis set, and for bismuth a segmented all-electron contracted DZP basis set constructed for use with the non-relativistic DHK Hamiltonian.

### **Term Values for SbH**<sub>2</sub>

Thus far, we have carried out calculations of rovibronic term values for  $\tilde{X}^2 B_1$  and  $\tilde{A}^2 A_1$  SbH<sub>2</sub> by means of the RENNER program system [2, 3, 4]. Values for  ${}^{121}$ SbH<sub>2</sub>,  ${}^{121}$ SbD<sub>2</sub>,  ${}^{121}$ SbHD,  ${}^{123}$ SbH<sub>2</sub>, <sup>123</sup>SbD<sub>2</sub>, and <sup>123</sup>SbHD are available, but we list only those for <sup>121</sup>SbH<sub>2</sub> here. Simulations of rovibronic spectra are under way.

Table 1: Calculated rovibron	c term values (in cm <sup>-</sup>	$^{-1}$ ) for selected (a	$(v_1, v_2, v_3)$ states
of $\tilde{X}^2 B_1$ <sup>121</sup> SbH <sub>2</sub> .		X	

$N_{K_aK_c}$	000	1	10	1	11	1	10
$(v_1, v_2, v_3)$	$F_1{}^a$	$F_2{}^a$	$F_1{}^a$	$F_2$	$F_1$	$F_2$	$F_1$
(0,0,0)	0.0	8.481	8.609	7.082	9.561	9.891	12.309
(0,1,0)	828.342	836.894	837.026	835.468	838.101	838.412	840.964
(0,2,0)	1652.531	1661.171	1661.307	1659.661	1662.461	1662.756	1665.452
(1,0,0)	1889.054	1897.388	1897.532	1896.021	1898.498	1898.787	1901.201
(0,0,1)	1892.106	1900.496	1900.627	1900.627	1901.535	1901.839	1904.250
(0,3,0)	2472.531	2481.264	2481.405	2478.926	2481.908	2482.182	2482.182
(1,1,0)	2702.607	2710.884	2711.150	2709.613	2712.242	2712.513	2715.063
(0,1,1)	2704.247	2712.710	2712.849	2711.386	2713.881	2714.155	2716.701
(0,4,0)	3290.569	3299.407	3299.551	3295.414	3298.596	3298.832	3301.843
(1,2,0)	3512.175	3520.732	3520.770	3519.162	3521.974	3522.215	3524.910
(0,2,1)	3512.176	3520.729	3520.860	3519.097	3521.991	3522.213	3524.902
(2,0,0)	3708.831	3717.135	3717.202	3715.650	3718.180	3718.402	3720.813
(1,0,1)	3709.349	3717.626	3717.703	3716.135	3718.673	3718.920	3721.330
(0,0,2)	3780.747	3789.015	3789.148	3787.581	3790.052	3790.320	3792.730
(0,5,0)	4102.517	4111.504	4111.657	4109.007	4112.417	4112.625	4115.818
(0,3,1)	4316.126	4324.782	4324.909	4322.225	4325.153	4325.480	4328.320
(1,3,0)	4317.675	4326.302	4326.492	4323.912	4326.916	4327.133	4329.983
(2,1,0)	4506.171	4514.542	4514.615	4513.023	4515.696	4515.913	4518.460
(1,1,1)	4506.455	4514.805	4514.900	4513.283	4515.976	4516.196	4518.742
(0,1,2)	4577.898	4586.237	4586.374	4584.770	4587.397	4587.642	4590.188
(0, 6, 0)	4905.680	4914.771	4914.932	4912.027	4915.694	4915.853	4919.248

<sup>*a*</sup>An  $F_2$  state has J = N - 1/2; an  $F_1$  state has J = N + 1/2.

**Table 2:** Calculated rovibronic term values<sup>*a*</sup> (in cm<sup>-1</sup>) for selected  $(v_1, v_2, v_3)$  states of  $\tilde{A}^2 A_1 {}^{121}$ SbH<sub>2</sub>.

$N_{K_aK_c}$	000	1	10	1	11	1	10
$(v_1, v_2, v_3)$	$F_1{}^b$	$F_2{}^b$	$F_1{}^b$	$F_2$	$F_1$	$F_2$	$F_1$
				$^{121}$ SbH $_2$			
(0,0,0)	18316.216 <sup>c</sup>	6.240	6.457	19.214	10.844	10.844	10.844
(0,1,0)	615.973	622.265	622.497	636.397	626.815	637.434	627.616
(0,2,0)	1275.968	1282.237	1282.237	1298.815	1286.940	1299.905	1287.716
(1,0,0)	1586.781	1592.887	1593.108	1605.927	1597.430	1606.818	1598.142
(0,0,1)	1627.291	1633.426	1633.646	1646.052	1637.825	1646.962	1638.558
(0,3,0)	1950.598	1956.822	1957.080	1977.582	1961.433	1978.695	1962.121
(1,1,0)	2194.131	2200.295	2200.530	2214.350	2204.726	2215.365	2205.503
(0,1,1)	2226.467	2232.659	2232.892	2246.377	2236.994	2247.400	2237.785
(0,4,0)	2604.237	2610.436	2610.641	2638.632	2614.033	2639.744	2614.574
(1,2,0)	2840.935	2847.077	2882.516	2863.555	2851.600	2864.626	2852.355
(0,2,1)	2871.873	2878.045	2878.300	2894.067	2882.516	2895.142	2883.284
(2,0,0)	3114.963	3120.942	3121.165	3133.929	3125.375	3134.800	3126.064
(1,0,1)	3133.207	3139.209	3139.432	3151.899	3143.541	3152.779	3144.244
(0,0,2)	3227.186	3233.207	3233.429	3245.647	3237.452	3246.538	3238.168
(0,5,0)	3244.770	3251.013	3251.137	3288.429	3252.341	3289.610	3252.782

<sup>*a*</sup>Unless otherwise indicated the term values are relative to the  $\tilde{A}^2 A_1$  level with  $(v_1, v_2, v_3, N_{K_aK_c}, J) = (0, 0, 0, 0_{00}, 1/2)$ . <sup>b</sup>An  $F_2$  state has J = N - 1/2; an  $F_1$ state has J = N + 1/2. <sup>c</sup>Relative to the  $\tilde{X}^2 B_1$  level with  $(v_1, v_2, v_3, N_{K_aK_c}, J) =$  $(0, 0, 0, 0_{00}, 1/2).$ 

# **Local Mode Vibrations and Energy Clusters**

![](_page_1_Figure_17.jpeg)

![](_page_1_Figure_18.jpeg)

The term values of Table 1 show that  $\tilde{X}^2 B_1$  SbH<sub>2</sub> is a local mode molecule. Stretching states  $(v_1, 0, v_3)$  with a common value of  $v_1$  +  $v_3 = N$  are close in energy and form characteristic patterns. The energy patterns are explained in terms of the Harmonically-Coupled-Anharmonic-Oscillator (HCAO) model (see Refs. [5, 6] and references therein), which sets up a Hamiltonian-representation matrix for a given value of N in terms of Morse-oscillator basis functions  $|n_1n_3\rangle$  with  $n_1$  $+ n_3 = N$ . The matrix elements depend on three parameters  $\omega_M$ ,  $x_M$ , and  $\lambda$ . Typically,  $\omega_M \gg x_M$  and  $\omega_M \gg \lambda$  (see Fig. 2). In reality, the characteristic patterns are sometimes 'spoiled' by interactions with nearby  $(v_1, v_2, v_3)$  states having  $v_2 > 0$ ; these states are not accounted for by the HCAO model.

The vibrational energy level clusters caused by local-mode effects are accompanied by rovibronic energy clusters at high rotational excitation [5, 6, 7], analogous to the ones formed in the  $X^2B_1$  and  $A^2A_1$ electronic states of the PH<sub>2</sub> radical [8]. Figure 3 shows examples of this; they are term value diagrams for the vibrational ground state (left), and the combined  $\nu_1/\nu_3$  states (right), respectively, of  $\tilde{X}^2 B_1$  <sup>121</sup>SbH<sub>2</sub>. In both displays, we recognize the formation of four-fold energy clusters, the states in each cluster being of symmetry  $A_1 \oplus A_2 \oplus B_1 \oplus$  $B_2$  [11] in the molecular symmetry group [9, 10]  $C_{2v}(M)$ . The energy clusters in Fig. 3(left) are of Type I [12]; they involve only one vibrational state, the vibrational ground state  $\tilde{X}^2 B_1$  <sup>121</sup>SbH<sub>2</sub>. The energy clusters in Fig. 3(right) are formed by coalescence (with increasing J) of two energy doublets, one doublet belonging to the  $\nu_1$  vibrational state and the other one to the  $\nu_3$  vibrational state. Such clusters are of Type II [12].

Molecu <sup>121</sup>SbH

 $^{121}$ SbD

<sup>121</sup>SbH

#### **Contact Information:**

FB C – Physikalische und Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany

Phone: +49 202 439 2468 Email: jensen@uni-wuppertal.de WWW: http://www.ptc.uni-wuppertal.de /jensen.html

![](_page_1_Figure_32.jpeg)

![](_page_1_Figure_33.jpeg)

#### Conclusions

ule	Environment	$\nu_3/\mathrm{cm}^{-1}$	$\nu_1/\mathrm{cm}^{-1}$
$[_{2}]$	pure $H_2$	1878	1869.7
_	Ne/H <sub>2</sub>	1883.9	1879.0
	$Ar/H_2$	1869.0	1863.7
	Calc.	1892.1	1889.1
2	pure $D_2$	1345.8	1341.9
	Ne/D <sub>2</sub>	1352.0	1349.4
	$Ar/D_2$	1341.8	1337.6
	Calc.	1360.6	1357.8
D	Ar/HD	1866.5	1339.6
	Calc.	1890.7	1359.0

In the matrix isolation infrared spectroscopic work of Ref. [13], laser ablated Sb atoms were reacted with hydrogen during condensation in six different environments: pure  $H_2$ , Ne/ $H_2$ , Ar/ $H_2$ , pure  $D_2$ , Ne/ $D_2$ , Ar/ $D_2$ , and Ar/HD. In each en-

vironment, two bands were identified as the stretching vibrational fundamentals of  $SbH_2$ ,  $SbD_2$ , or SbHD. In the table, we have sum-

![](_page_1_Picture_38.jpeg)

marized the experimental results and compared them to our predicted fundamental wavenumbers, which obviously support the assignments. A spectrum attributed to the absorption spectrum of SbH<sub>2</sub> ( $A \leftarrow X$ ) was obtained in Ref. [14] by the flash photolysis of stibine (SbH<sub>3</sub>). Also, in Ref. [15] the emission spectrum of SbH<sub>2</sub> ( $A \rightarrow X$ ) from 400 to 700 nm was recorded with a resolution of 12Å, and a portion of the spectrum from 480 to 530 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.

as a  $^{2}\Delta_{g}$  state.

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![](_page_1_Figure_58.jpeg)

![](_page_1_Figure_59.jpeg)

**Figure 4:**  $\rho = 180^{\circ} - \angle$ (H–Bi–H). At linearity ( $\rho = 0$ ), the  $\tilde{X}^2 B_1$  and  $\tilde{A}^2 A_1$  states become degenerate as a  ${}^{2}\Pi_{u}$  state, while the  $2{}^{2}A_{1}$  and  $3{}^{2}B_{1}$  states become degenerate

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