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An *ab initio* study of the Renner effect and spin-orbit coupling in SbH₂ and BiH₂

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Introduction

We present the results of *ab initio* calculations for the two lowest electronic states of the Group 15 (pnictogen) dihydrides, SbH₂ and BiH₂. For each of these molecules the two lowest electronic states, \tilde{X}^2B_1 and \tilde{A}^2A_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 SbH₂. Including both the Renner effect and spin-orbit coupling, we calculate rovibronic term values for SbH₂. For the heavier dihydride BiH₂ we calculate bending potential curves and the spin-orbit coupling constant for comparison.

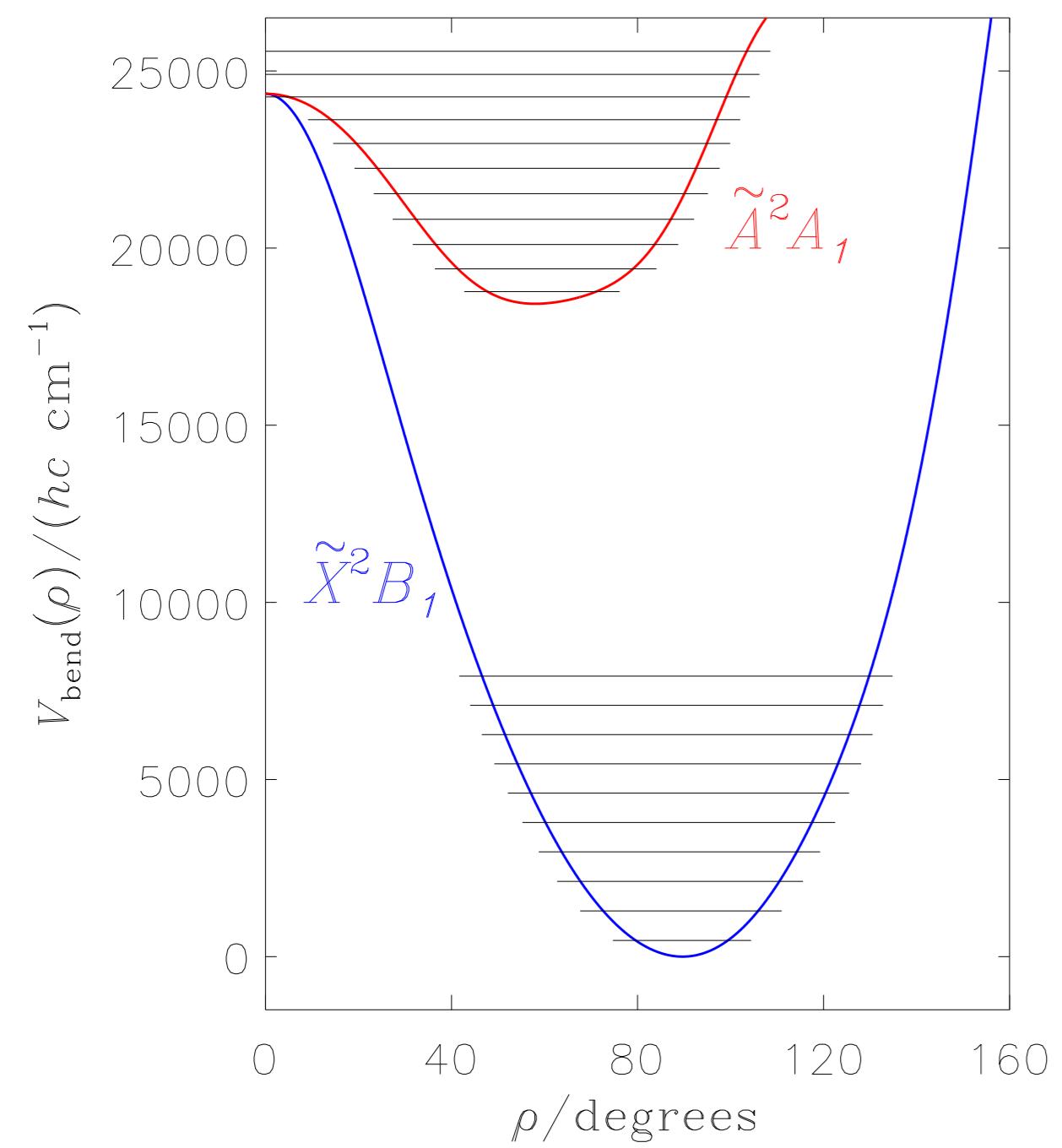


Figure 1: The bending potential energy functions of SbH₂ in the \tilde{X}^2B_1 and \tilde{A}^2A_1 electronic states. The bond lengths are both held fixed at the value $r^{(\text{ref})} = 1.719 \text{ \AA}$. The energies of the lowest bending eigenstates with $K_a = 0$ are indicated for the two electronic states. $p = 180^\circ - \angle(\text{H-Sb-H})$.

Ab initio Calculations

We have computed energies on the potential energy surfaces of the \tilde{X}^2B_1 and \tilde{A}^2A_1 electronic states of SbH₂ and BiH₂ with the MOLPRO 2010.1 program package [1], employing an all-electron CASSCF method, followed by a MRCI treatment. For hydrogen we used a aug-cc-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 SbH₂

Thus far, we have carried out calculations of rovibronic term values for \tilde{X}^2B_1 and \tilde{A}^2A_1 SbH₂ by means of the RENNER program system [2, 3, 4]. Values for ¹²¹SbH₂, ¹²¹SbD₂, ¹²¹SbHD, ¹²³SbH₂, ¹²³SbD₂, and ¹²³SbHD are available, but we list only those for ¹²¹SbH₂ here. Simulations of rovibronic spectra are under way.

Table 1: Calculated rovibronic term values (in cm^{-1}) for selected (v_1, v_2, v_3) states of \tilde{X}^2B_1 ¹²¹SbH₂.

(v_1, v_2, v_3)	$N_{K_a K_c}$	0_{00}	1_{10}	F_1^a	F_2^a	F_1^a	F_2^a	F_1^a	F_2^a	F_1^a
(0,0,0)	0	0.0		8.481	8.609	7.082	9.561	9.891	12.309	
(0,1,0)	828.342	836.894	837.026	835.466	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	2478.929	2481.182	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	3299.531	3295.414	3298.596	3298.832	3301.843			
(1,2,0)	3512.175	3520.732	3520.770	3519.163	3521.974	3522.215	3524.910			
(0,2,1)	3512.175	3520.729	3520.860	3519.097	3521.991	3522.213	3524.902			
(2,0,0)	3708.831	3717.135	3717.202	3715.650	3718.308	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	3784.174	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			

Table 2: Calculated rovibronic term values^a (in cm^{-1}) for selected (v_1, v_2, v_3) states of \tilde{A}^2A_1 ¹²¹SbH₂.

(v_1, v_2, v_3)	$N_{K_a K_c}$	0_{00}	1_{10}	F_1^b	F_2^b	F_1^b	F_2^b	F_1^b	F_2^b	F_1^b
(0,0,0)	1831.216 ^c	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	2204.724	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			

^aUnless otherwise indicated the term values are relative to the \tilde{A}^2A_1 level with $(v_1, v_2, v_3, N_{K_a K_c}, J) = (0, 0, 0, 0, 0, 1/2)$. ^bAn F_2 state has $J = N - 1/2$; an F_1 state has $J = N + 1/2$. ^cRelative to the \tilde{X}^2B_1 level with $(v_1, v_2, v_3, N_{K_a K_c}, J) = (0, 0, 0, 0, 1/2)$.

Local Mode Vibrations and Energy Clusters

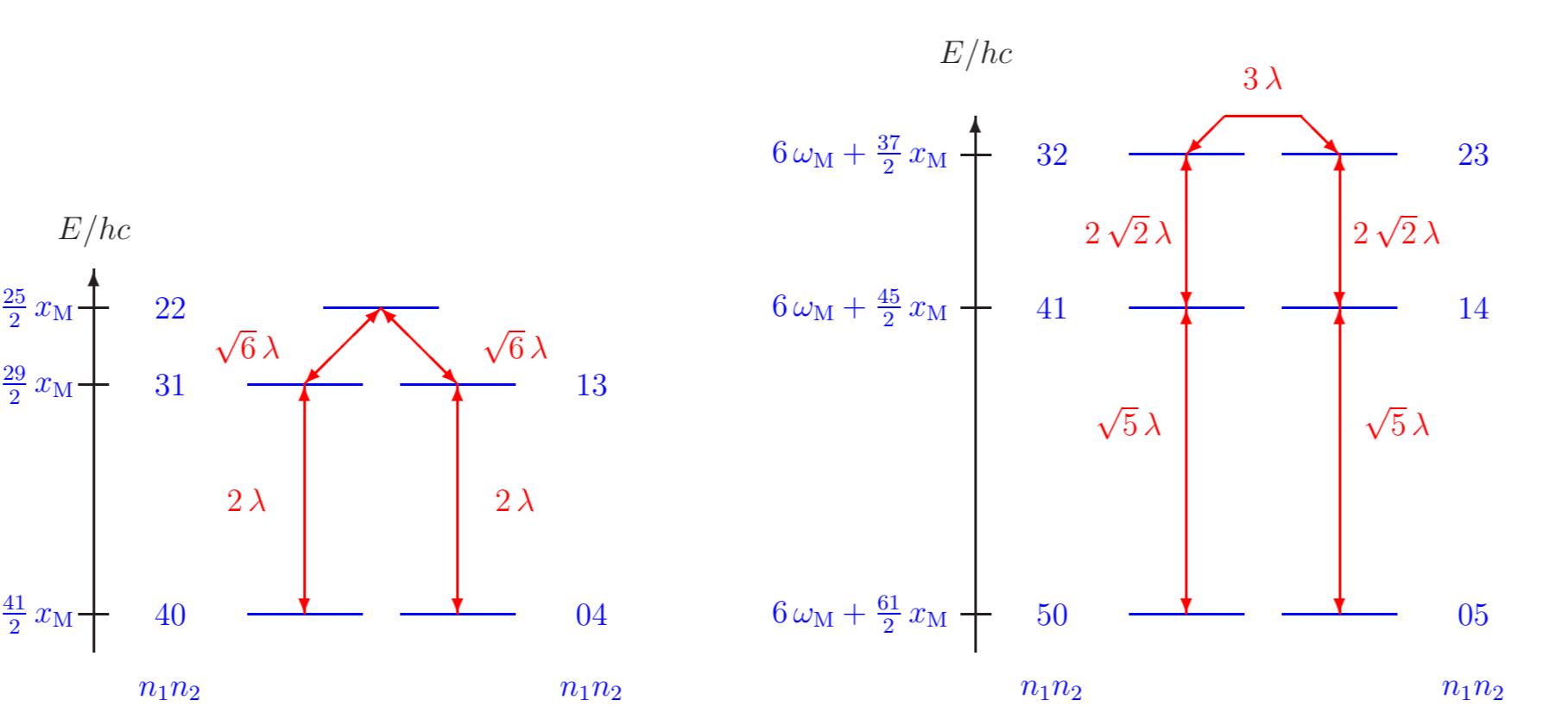


Figure 2: Schematic representation of the Harmonically-Coupled-Anharmonic-Oscillator (HCAO) energy matrix for $v_1 + v_3 = n_1 + n_3 = 4$ (left) and 5 (right). The horizontal lines represent the diagonal matrix elements and the off-diagonal elements are indicated. Note that by definition, the parameter $x_M < 0$.

The term values of Table 1 show that \tilde{X}^2B_1 SbH₂ 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

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