

# SbH<sub>2</sub> and BiH<sub>2</sub>

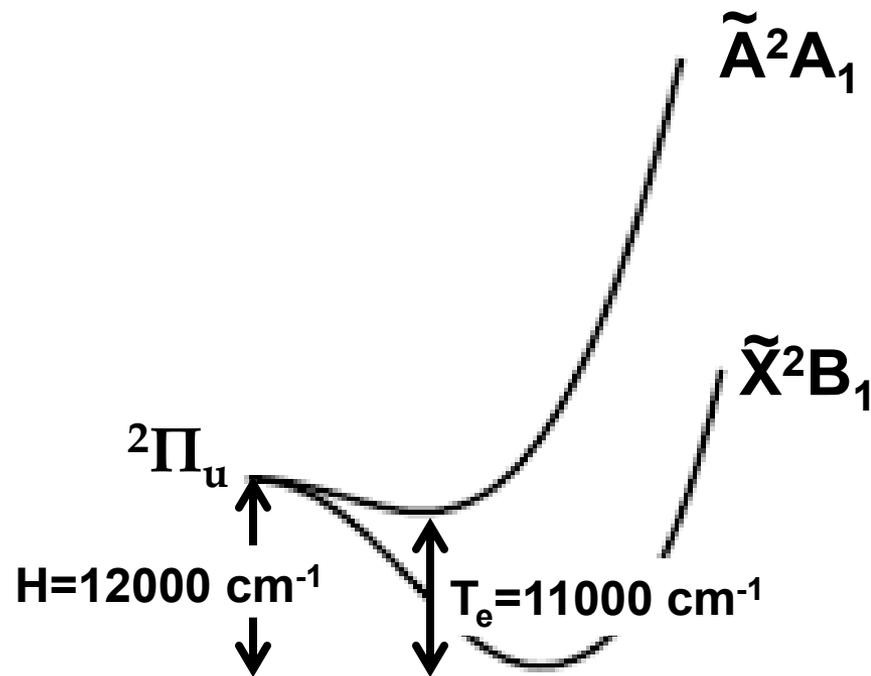
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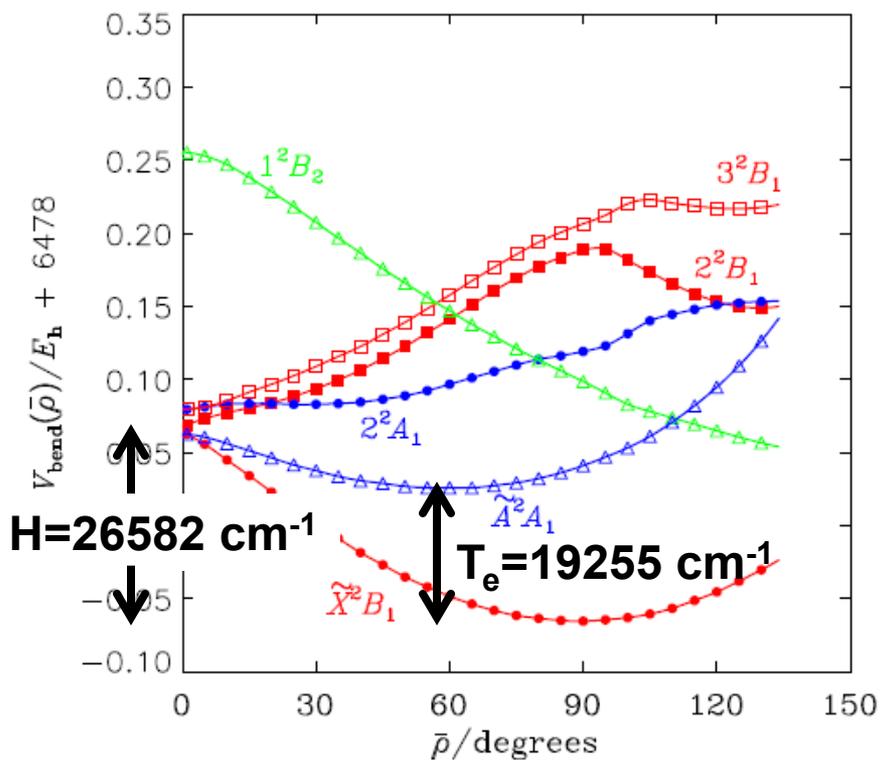
# NH<sub>2</sub> Renner Effect



# Bending cuts through the lowest six potentials using CAS-SCF MRCI for the full 3d surfaces

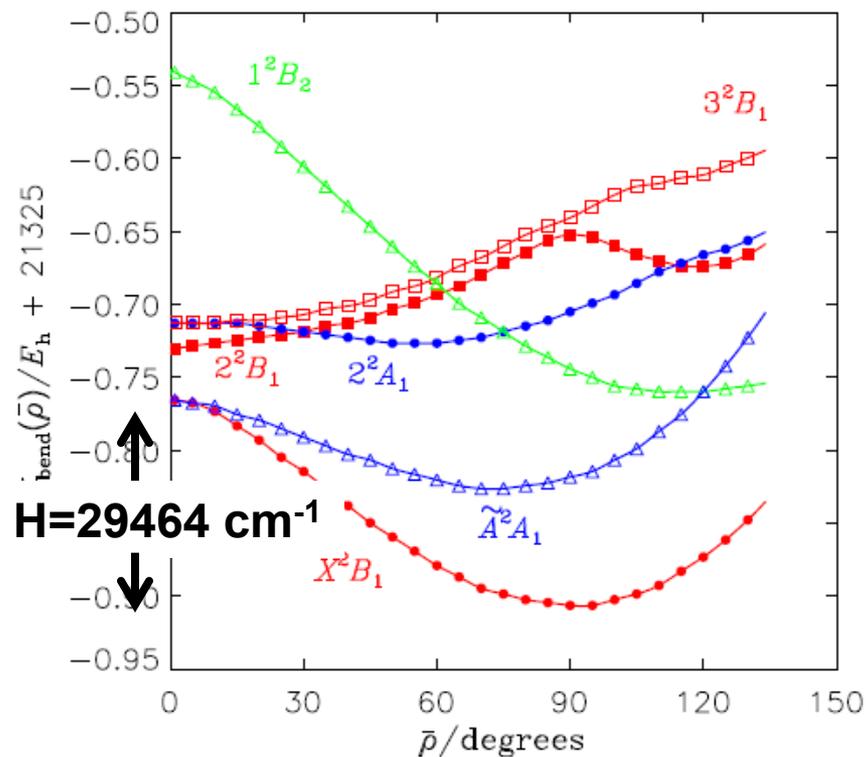
**SbH<sub>2</sub>**

**R = 1.719 Å**



**BiH<sub>2</sub>**

**R = 1.803 Å**



**H=26470 cm<sup>-1</sup> T<sub>e</sub>=19478 cm<sup>-1</sup> ← CCSD(T) a better ab initio method**

From now on we only talk about  $\text{SbH}_2$

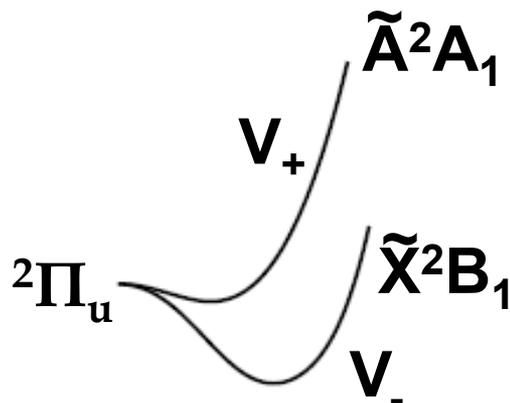
3d potential energy surfaces,  $V_+$  and  $V_-$

3d dipole moment surfaces,  $\mu_y$  and  $\mu_z$  for each state

3d transition moment surface,  $\mu_x$

**$\text{SbH}_2$ :**

CAS-SCF MRCI  
124 geometries



$\text{NH}_2$      $H \sim 12000 \text{ cm}^{-1}$      $T_e \sim 11000 \text{ cm}^{-1}$

$\text{SbH}_2$      $H = 26582 \text{ cm}^{-1}$      $T_e = 19255 \text{ cm}^{-1}$

$T_e = 19478 \text{ cm}^{-1}$     **CCSD(T)**

## 3-dimensional potential energy surfaces $V_+$ and $V_-$

$$V_{\pm} = \sum_{jkl} \mathbf{G}_{jkl}^{(\pm)} (y_1)^j (y_3)^k (1 - \cos \rho)^l$$

where  $y_i = 1 - \exp(-a\Delta r_{i2})$   $i = 1$  or  $3$

$-(+)$  = *X(A) state*

$$\mathbf{G}_{jk0}^{(+)} = \mathbf{G}_{jk0}^{(-)} \text{ so that } V_+ = V_- \text{ when } \rho = 0$$

52 Parameters fitted to energies at 124 geometries for  $\text{SbH}_2$

Diagonalize  $T_{\text{rve}} + V_{\pm}$  in an MO-RB basis set for each state

# The Renner Effect

$$T_{\text{rot}}^{(z)} = A[N_z - L_z]^2$$

$$= A[N_z^2 - 2N_zL_z + L_z^2]$$

As  $\rho \rightarrow 0$   
 $A \rightarrow \infty$

$K^2$

$2K \langle X | L_z | A \rangle$

$\Lambda^2$

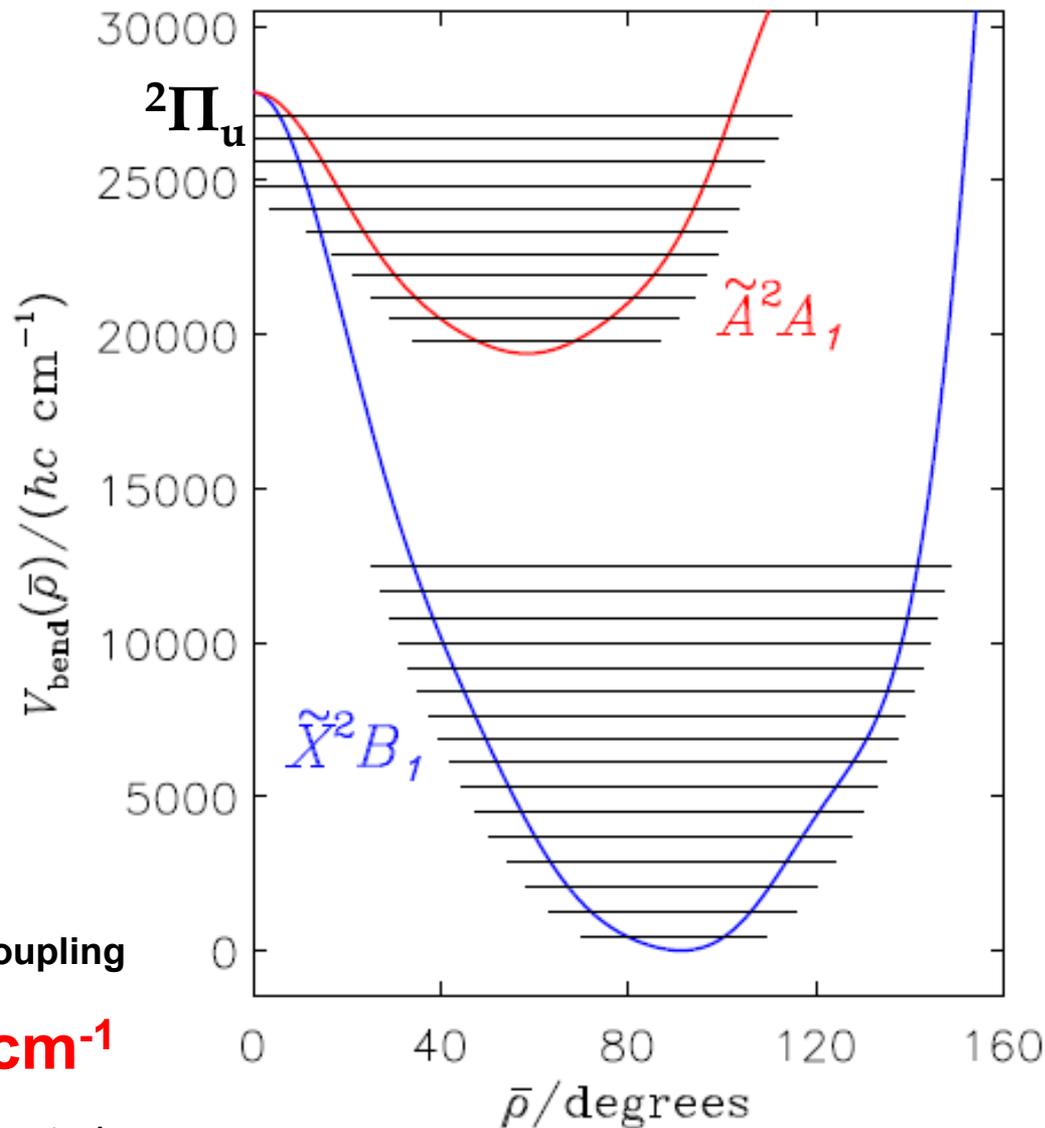
$i\Lambda$

For  $\text{SbH}_2$   $\Lambda = 1$

This is dealt  
 with as an  
 afterthought

$$+ H_{\text{SO}} = A_{\text{SO}} L_z S_z$$

# A cut through our 3d PE surfaces ( $R = 1.719 \text{ \AA}$ ) and the calculated vibrational levels for $\text{SbH}_2$



Then add spin-orbit coupling

$$A_{\text{SO}} = 2528 \text{ cm}^{-1}$$

(using Breit-Pauli operator)

Table 3: Calculated rovibronic term values (in  $\text{cm}^{-1}$ ) for selected  $(v_1, v_2, v_3)$  states  $\tilde{X}^2B_1$   $^{121}\text{SbH}_2$ .

$N_{K_a K_c}$ $(v_1, v_2, v_3)$	0 <sub>00</sub>		1 <sub>01</sub>		1 <sub>11</sub>		1 <sub>10</sub>	
	$F_1^a$	$F_2^a$	$F_1^a$	$F_2$	$F_1$	$F_2$	$F_1$	
(0,0,0)	0.000	8.582	8.656	7.442	9.318	10.330	12.174	
(0,1,0)	805.280	813.809	813.885	812.861	814.915	815.757	817.763	
(0,2,0)	1628.326	1636.911	1636.987	1635.792	1637.979	1638.809	1640.933	
(0,0,1)	1873.416	1881.916	1881.985	1880.784	1882.579	1883.657	1885.427	
(1,0,0)	1876.016	1884.482	1884.558	1883.397	1885.221	1886.241	1888.034	
(0,3,0)	2461.525	2470.214	2470.288	2468.170	2470.479	2471.358	2473.587	
(1,1,0)	2675.052	2683.314	2683.509	2682.518	2684.531	2685.361	2687.320	
(0,1,1)	2676.013	2684.449	2684.513	2683.687	2685.542	2686.404	2688.338	
(0,4,0)	3292.532	3301.383	3301.449	3297.996	3300.430	3301.404	3303.734	
(1,2,0)	3493.939	3502.316	3502.439	3500.977	3503.116	3503.927	3506.009	
(0,2,1)	3495.061	3503.541	3503.616	3503.137	3505.201	3506.017	3508.071	
(1,0,1)	3702.653	3711.095	3711.067	3710.732	3712.544	3713.574	3715.297	
(0,0,2)	3703.407	3711.807	3711.814	3710.549	3712.400	3713.442	3715.169	
(2,0,0)	3749.703	3758.072	3758.137	3756.820	3758.573	3759.631	3761.354	
(0,5,0)	4105.994	4115.114	4115.174	4112.392	4114.959	4116.113	4118.548	
(1,3,0)	4321.482	4330.008	4330.088	4328.238	4330.470	4331.365	4333.554	
(0,3,1)	4322.372	4330.973	4331.077	4332.742	4334.969	4335.832	4337.991	
(1,1,1)	4498.581	4507.035	4506.930	4508.990	4510.911	4511.750	4513.639	
(0,1,2)	4499.377	4507.648	4507.728	4506.707	4508.820	4509.657	4511.554	
(2,1,0)	4551.161	4559.465	4559.525	4557.679	4559.611	4560.469	4562.354	
(0,6,0)	4888.896	4898.347	4898.407	4896.833	4899.538	4900.950	4903.494	
(1,4,0)	5138.520	5147.196	5147.285	5145.736	5148.229	5149.125	5151.417	
(0,4,1)	5138.564	5147.366	5147.333	5149.832	5152.169	5153.178	5155.438	
(1,2,1)	5309.909	5318.288	5318.294	5321.756	5323.824	5324.651	5326.657	
(0,2,2)	5310.437	5318.772	5318.835	5317.552	5319.689	5320.496	5322.515	
(2,2,0)	5366.482	5374.845	5374.899	5373.003	5375.069	5375.913	5377.914	
(1,0,2)	5488.570	5496.807	5496.865	5496.094	5497.801	5498.877	5500.546	
(0,0,3)	5498.515	5506.768	5506.810	5507.157	5508.847	5509.919	5511.574	
(2,0,1)	5586.152	5594.445	5594.474	5593.229	5595.066	5596.054	5597.688	
(3,0,0)	5586.375	5594.627	5594.508	5593.096	5594.813	5595.839	5597.505	
(0,7,0)	5648.348	5658.131	5658.190	5655.396	5658.269	5659.897	5662.572	
(0,5,1)	5936.703	5945.837	5945.730	5943.718	5946.113	5947.476	5949.856	
(1,5,0)	5938.417	5947.446	5947.619	5945.164	5947.872	5948.948	5951.354	

Vibrational level clustering of stretching excited states

Rotational level clustering at high J

A good local mode molecule

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

# Rotational energy level clustering at very high J-values in the $\tilde{X}^2B_1$ state of $SbH_2$

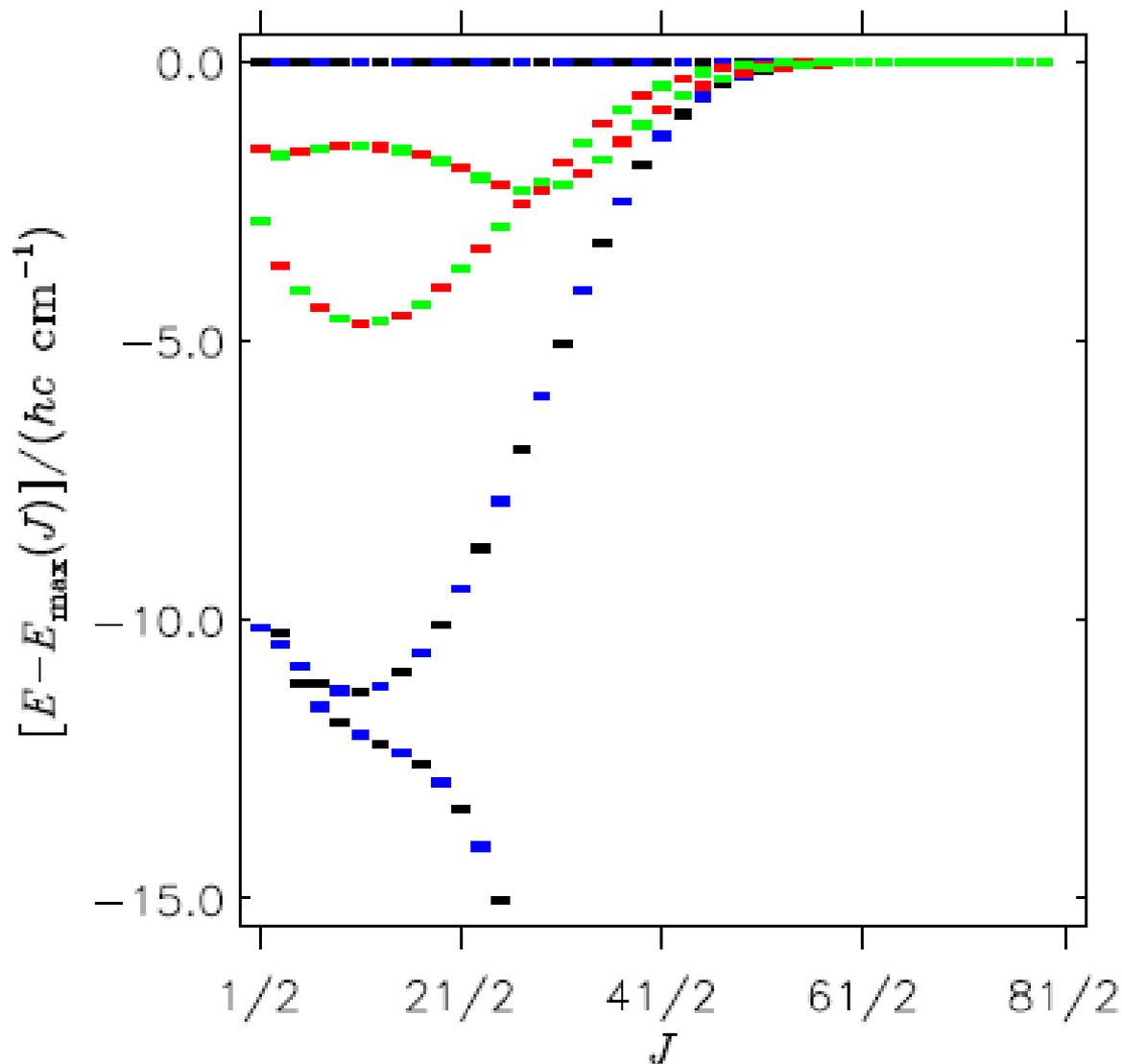
$N_{K_a K_c}$	$0_{00}$	$1_{01}$		$1_{11}$		$1_{10}$	
$(v_1, v_2, v_3)$	$F_1^a$	$F_2^a$	$F_1^a$	$F_2$	$F_1$	$F_2$	$F_1$
$(0,0,0)$	0.000	8.582	8.656	7.442	9.318	10.330	12.174

**J = 1/2 term values**

**Rovibronic symmetry**

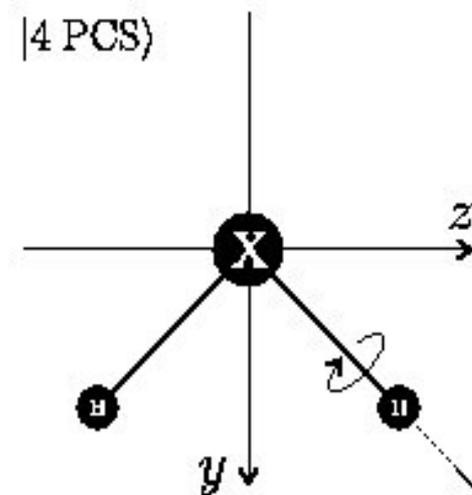
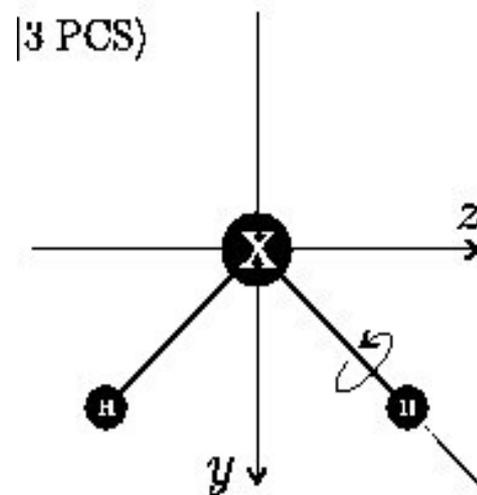
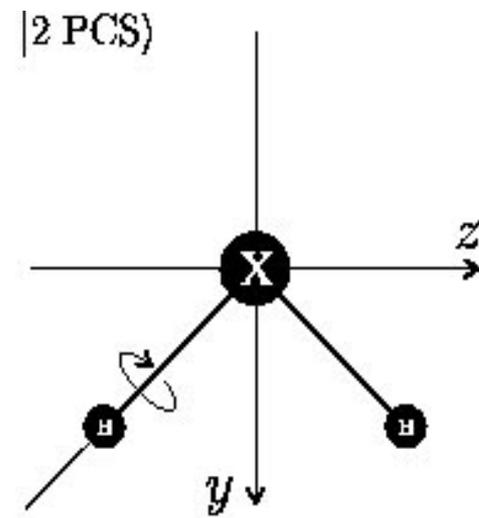
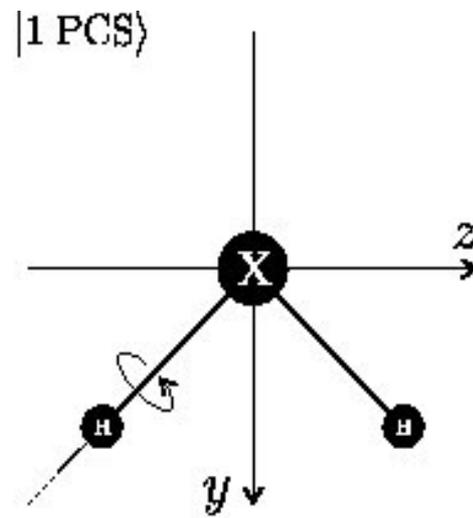


# Rotational energy level clustering at very high J-values



Red  $A_1$   
Black  $A_2$   
Blue  $B_1$   
Green  $B_2$

# Four localized Primitive Cluster States



<b><math>J = 0</math></b>	<b>MORBID</b>	<b>RENNER</b> <b><math>A_{SO} = 0</math></b>
(010)	806.19	806.20
(020)	1628.87	1628.90
(001)	1871.69	1871.64
(100)	1874.88	1874.84
(030)	2459.12	2459.17
(110)	2673.45	2673.42
(011)	2674.05	2674.01
(040)	3282.77	3282.85
(120)	3488.07	3488.06
(021)	3488.79	3488.77
(101)	3699.13	3699.07
(200)	3699.83	3699.75
(002)	3745.29	3745.20
(050)	4088.86	4088.97
(0,15,0)	11755.03	11744.98

	<b>MORBID</b>	<b>RENNER</b> $A_{SO} = 0$
<b>(000)</b> $1_{10}$	11.643	11.643
$1_{11}$	8.730	8.730
$1_{01}$	8.640	8.640
$2_{20}$	34.921	34.921
$2_{02}$	23.088	23.088
$5_{50}$	174.316	174.313
$5_{05}$	100.639	100.639
$10_{10,0}$	635.585	635.551
$10_{0,10}$	344.092	344.098

**Effect of  $-2AN_zL_z + AL_z^2$**

## Also calculate dipole and transition moment surfaces

The two dipole moment surfaces for each electronic state of  $\text{SbH}_2$  and transition moment surface between two electronic states of  $\text{SbH}_2$  were obtained at the CAS-MRCISD level in the framework of the  $C_s$  point group.

<b>X-state dipole moments at equilibrium</b>	<b><math>\text{SbH}_2</math></b>	<b>0.02 D</b>
	<b><math>\text{BiH}_2</math></b>	<b>0.62 D</b>

To understand the trend in dipole moments Peter made scalar relativistic MP2 calculations using double-zeta quality basis sets to obtain:

$\text{NH}_2$	$\text{PH}_2$	$\text{AsH}_2$	$\text{SbH}_2$	$\text{BiH}_2$
-2.32	-1.14	-0.54	+0.06	+0.72

<b>Mulliken charges</b>	<b>N -0.48</b>			<b>Bi +0.12</b>
	<b>H +0.24</b>			<b>H -0.06</b>

As go from N to Bi the electronegativity goes down

# Simulation of SbH<sub>2</sub> absorption spectrum, 0 to 5000 cm<sup>-1</sup>

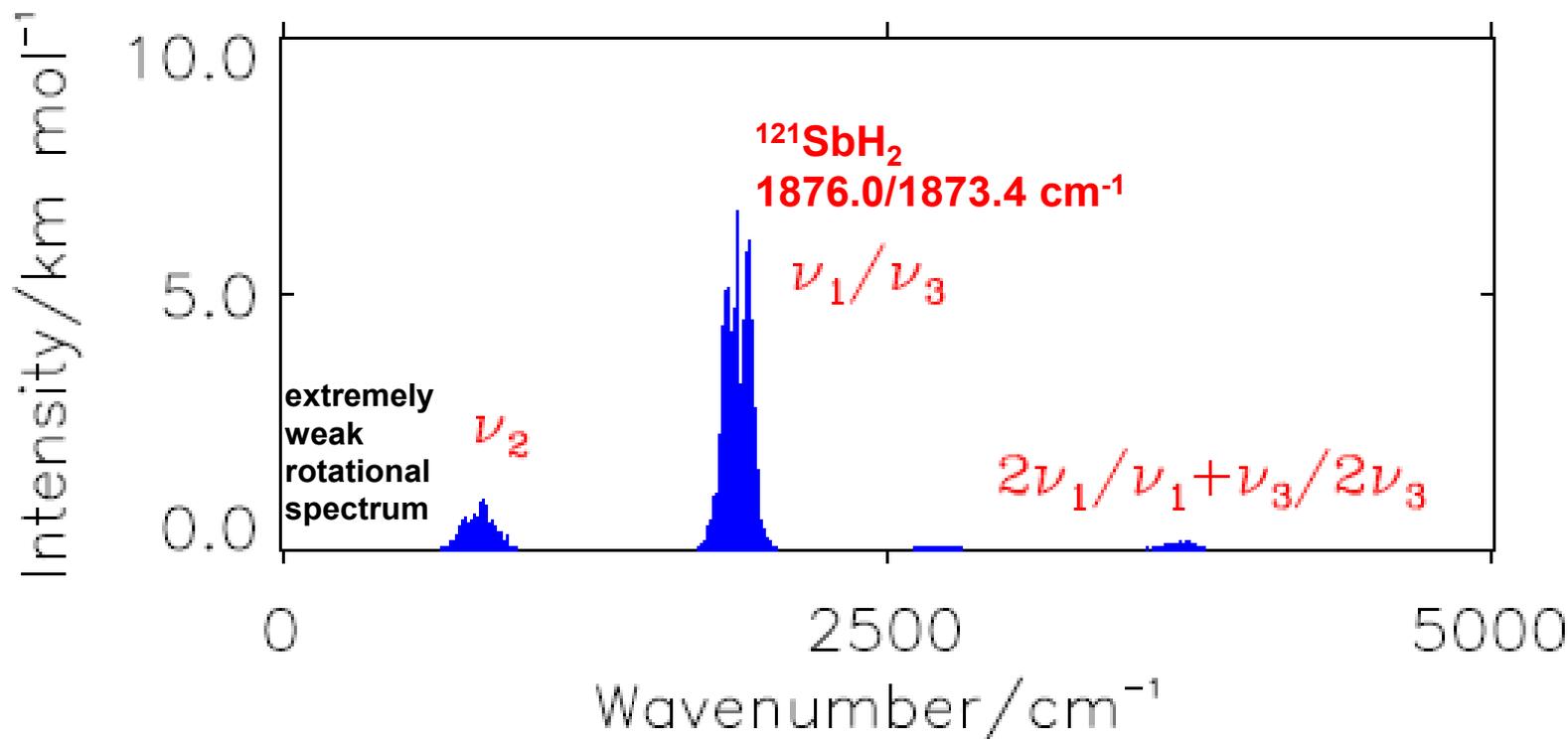


Figure 4: The infrared absorption spectrum of  $\tilde{X}^2B_1$   $^{121}\text{SbH}_2$  and  $^{123}\text{SbH}_2$  in natural abundance, simulated at a temperature of  $T = 300$  K. States with  $J \leq 19/2$  are taken into account.

**NOW TO THE COMPARISON WITH EXPERIMENT**

## Stretching fundamental term values for X-state

Molecule	Environment	$\nu_1/\text{cm}^{-1}$	$\nu_3/\text{cm}^{-1}$
SbH <sub>2</sub>	pure H <sub>2</sub>	1869.7	1878
	Ne/H <sub>2</sub>	1879.0	1883.9
	Ar/H <sub>2</sub>	1863.7	1869.0
<sup>121</sup> SbH <sub>2</sub>	Calc. <sup>a</sup>	1876.0	1873.4
SbD <sub>2</sub>	pure D <sub>2</sub>	1341.9	1345.8
	Ne/D <sub>2</sub>	1349.4	1352.0
	Ar/D <sub>2</sub>	1337.6	1341.8
<sup>121</sup> SbD <sub>2</sub>	Calc. <sup>b</sup>	1342.7	1340.5
SbHD	Ar/HD	1339.6	1866.5
<sup>121</sup> SbHD	Calc. <sup>c</sup>	1341.9	1874.0

$\nu_1 > \nu_3$

**Matrix isolation infrared spectrum obtained by reacting laser ablated Sb with hydrogen.**

**Wang, Souter and Andrews, JPCA, 107, 4244 (2003)**

**Experiment has  $\nu_3 > \nu_1$  from NH<sub>2</sub>**

**$\Delta K$  0  $\pm 1$**

**a-type b-type**

**Need  
Rotational  
resolution**

# Visible absorption spectrum of Flash-photolysis of SbH<sub>3</sub>

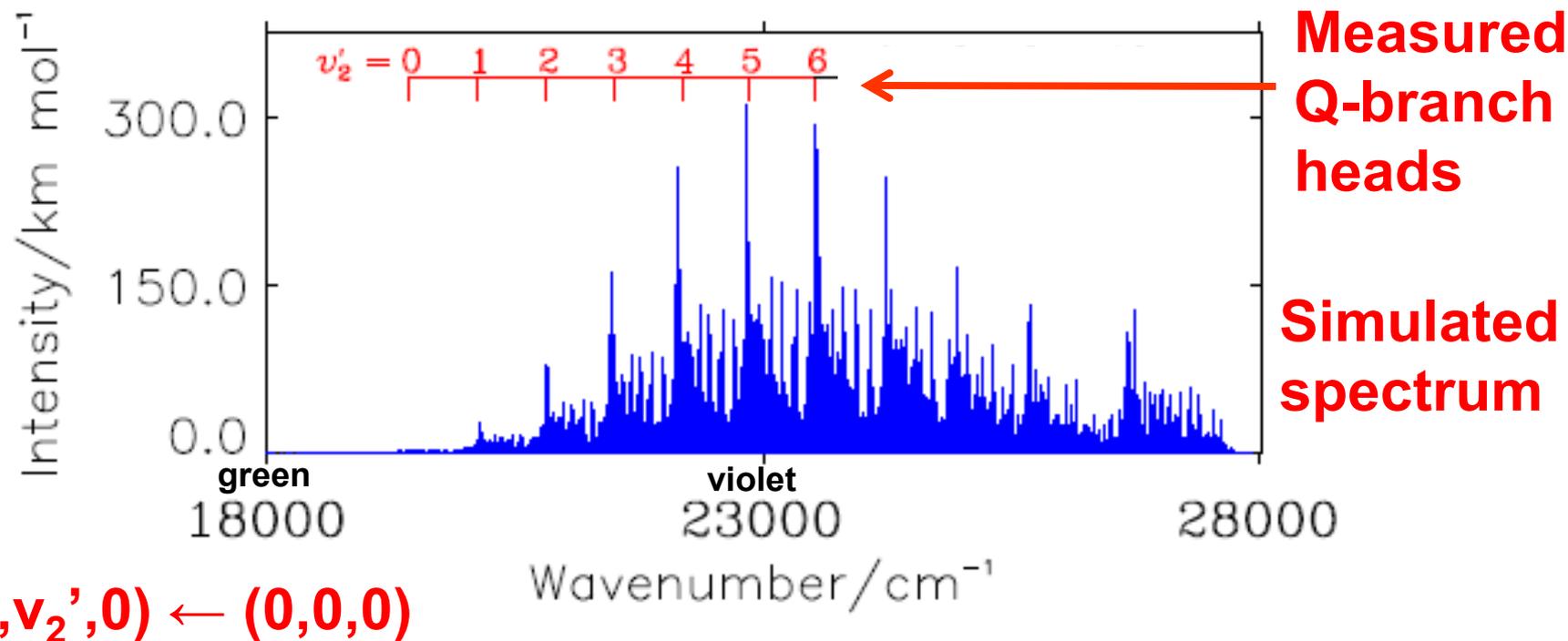


Figure 5: The  $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$  electronic absorption spectrum of <sup>121</sup>SbH<sub>2</sub> and <sup>123</sup>SbH<sub>2</sub> in natural abundance, simulated at a temperature of  $T = 300$  K. States with  $J \leq 19/2$  are taken into account. The experimentally determined Q-branch-head positions [20] for the vibronic bands  $\tilde{A}(0, v'_2, 0) \leftarrow \tilde{X}(0, 0, 0)$  ( $v'_2 = 0, 1, \dots, 6$ ; see Table 8) are indicated by the red part of the wavenumber comb,

**The visible absorption spectrum obtained by flash photolysis of stibine (SbH<sub>3</sub>).**  
**Basco and Lee, Spectrosc. Lett. 1, 13 (1968)**

Table 8: Experimentally observed Q-head positions  $\tilde{\nu}_{\text{obs}}$  ( $\text{cm}^{-1}$ ) in the  $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$  absorption spectrum of  $\text{SbH}_2$  [20] compared to vibronic energy spacings  $\tilde{\nu}_{\text{calc}}$  ( $\text{cm}^{-1}$ ) of  $^{121}\text{SbH}_2$ .

$(v_2')^a$	$\tilde{\nu}_{\text{obs}}$	$\tilde{\nu}_{\text{calc}}^b$	O-C <sup>c</sup>
0	19438	19459.8	-22
1	20131	20156.4	-25
2	20822	20827.7	-6
3	21511	21480.6	30
4	22191	22147.1	44
5	22863	22843.6	19
6	23529	23539.8	-11
7		24244.3	
8		24961.5	
9		25675.1	
10		26669.9	

**BUT THE ABOVE USES  $T_e$  (CAS-SCF MRCI) = 19255  $\text{cm}^{-1}$**

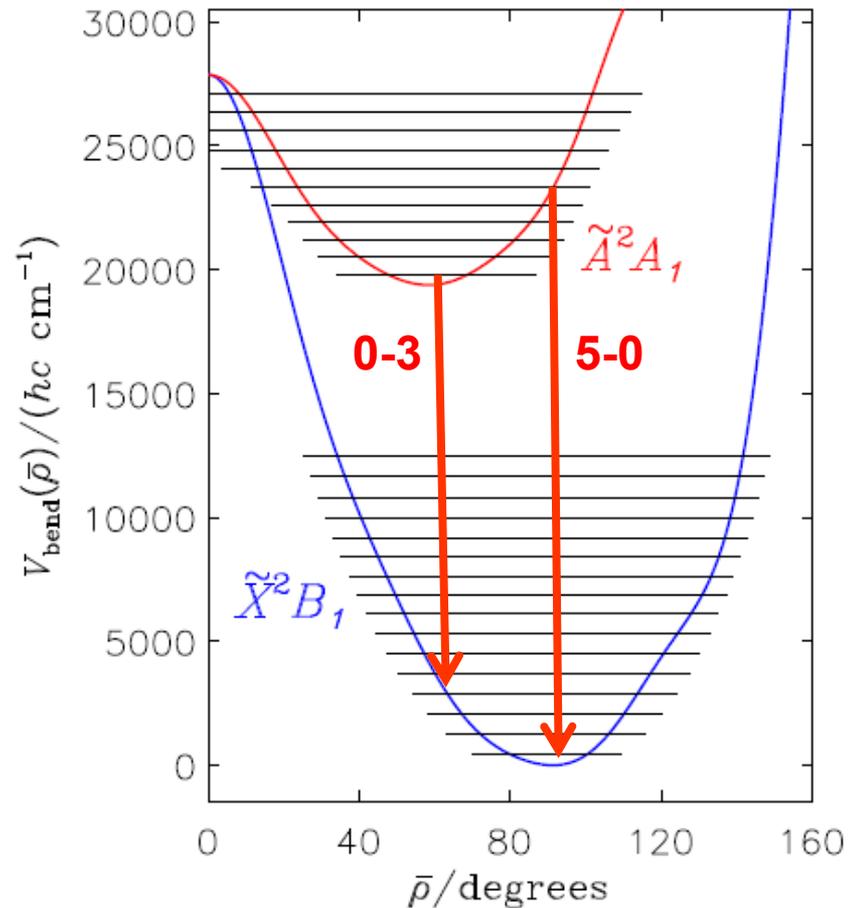
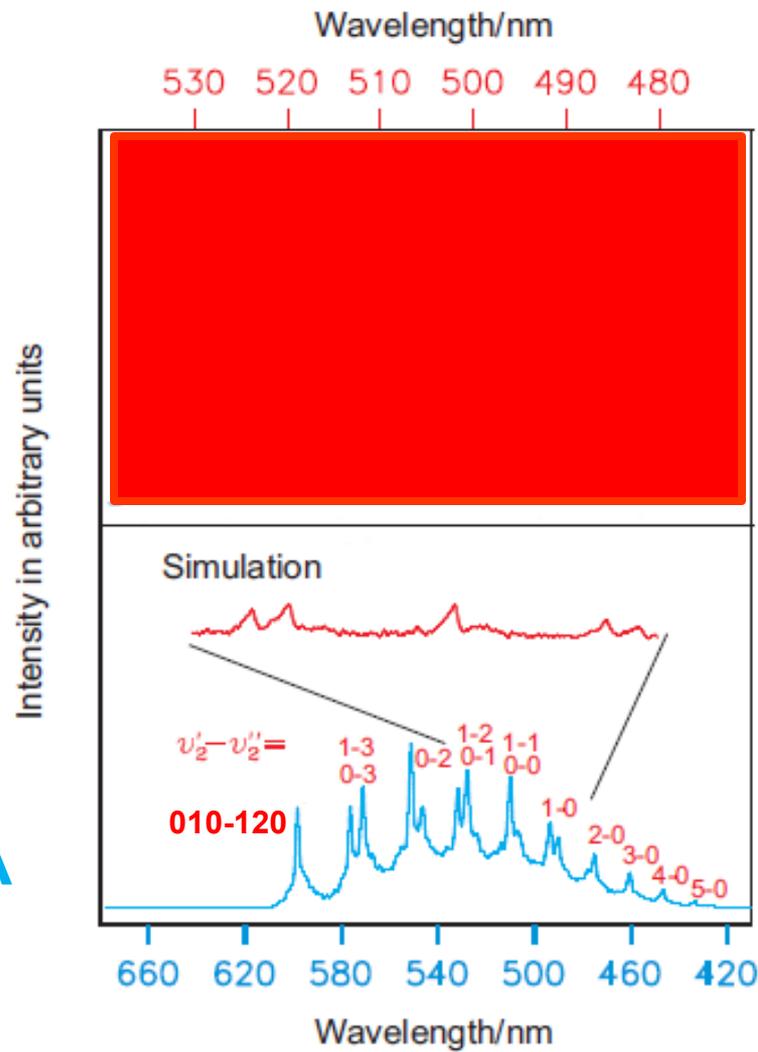
**AND WE KNOW  $T_e$  (CCSD(T)) = 19478  $\text{cm}^{-1}$**

**It's what you call "fortuitous"**

# Simulation of emission spectrum.

3 Å

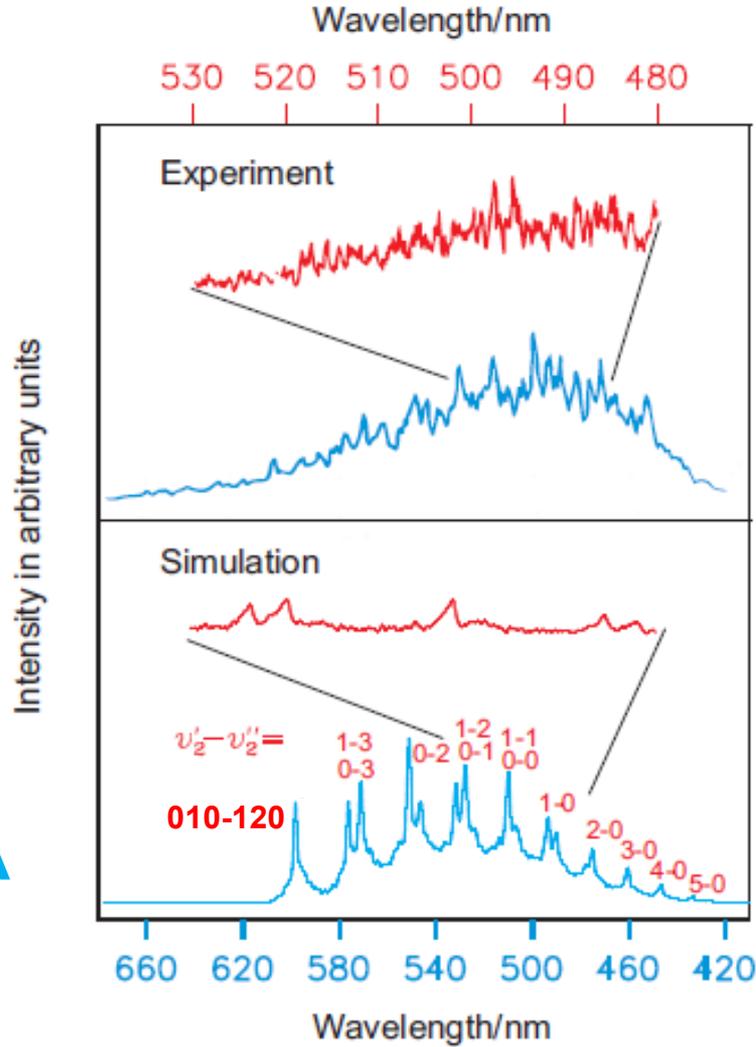
12 Å



Simulation temperature = 1200 K  
for predominantly A-state levels.  $J(\text{max}) = 49/2$

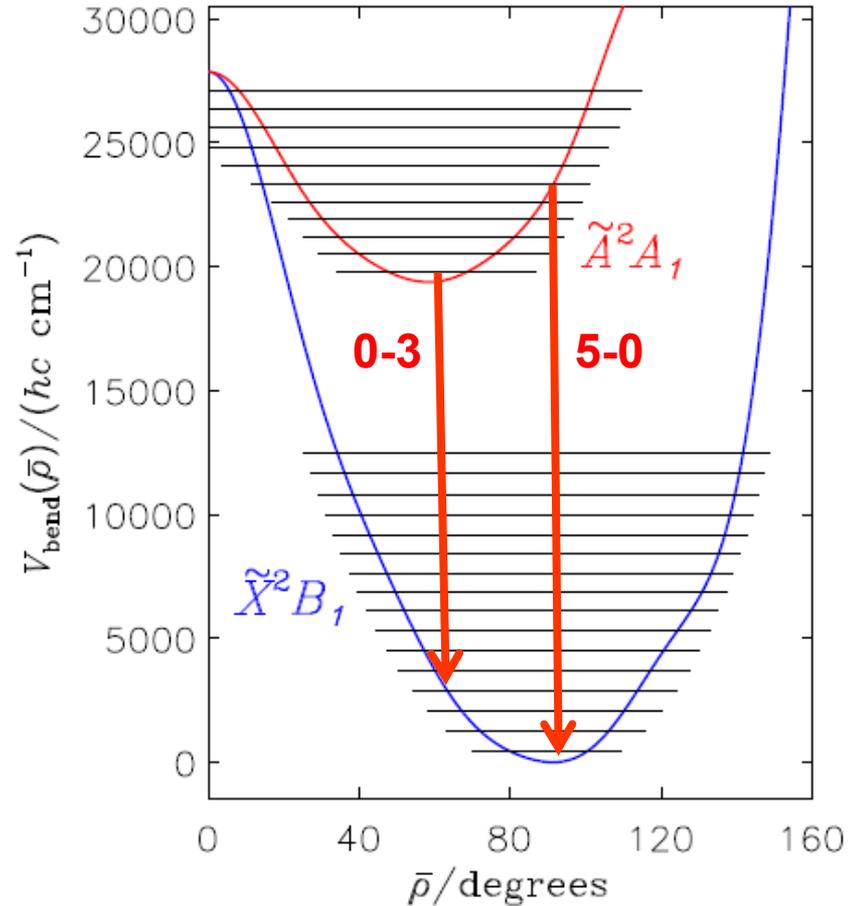
The visible emission spectrum obtained by  
UV laser photolysis of stibine.

Ni, Yu, Ma and Kong, CPL 128, 270 (1986)



3 Å

12 Å



Simulation temperature = 1200 K  
for predominantly A-state levels.  $J(\text{max}) = 49/2$



**Auckland North Shore Campus of Massey University**

## Ab Initio method used for full surfaces. CAS-SCF MRCI

We have computed energies on the potential energy surfaces of the  $\tilde{X}^2B_1$  and  $\tilde{A}^2A_1$  electronic states of  $\text{SbH}_2$  and  $\text{BiH}_2$  employing an all-electron complete active space self-consistent field (CASSCF) method [23, 24], followed by a multi-reference configuration interaction (MRCI) treatment [25, 26, 27]. For hydrogen we used a aug-cc-pV5Z basis set, [28] for antimony a Sapporo-DKH3-QZP-2012 basis set (extracted from the Sapporo Data Base of Segmented Gaussian Basis Sets [29]), and for bismuth a segmented all-electron contracted double zeta valence plus polarization function (DZP) basis set [30] constructed for use in conjunction with the non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonian

## Better method for H and $T_e$ as a check for $\text{SbH}_2$ . CCSD(T)

In order to check the precision of our *ab initio* method we performed scalar relativistic Douglas-Kroll CCSD(T) calculations using augmented correlation consistent quadruple basis sets for Sb [35] and H [36].