

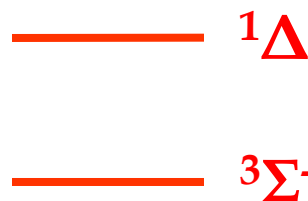
# The Group 15 (Pnictogen) Hydrides

(NPA**s**SbBi)

Group→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

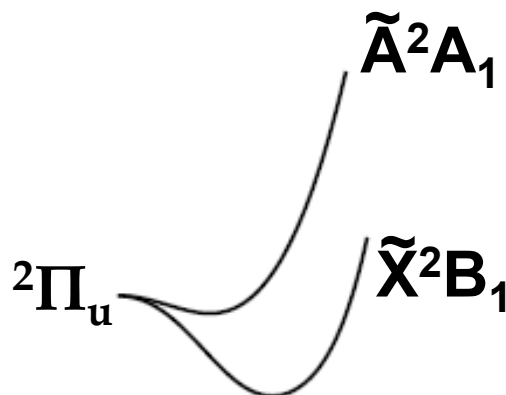
# The Group 15 (N-P-As-Sb-Bi) Hydrides

**Monohydrides:**



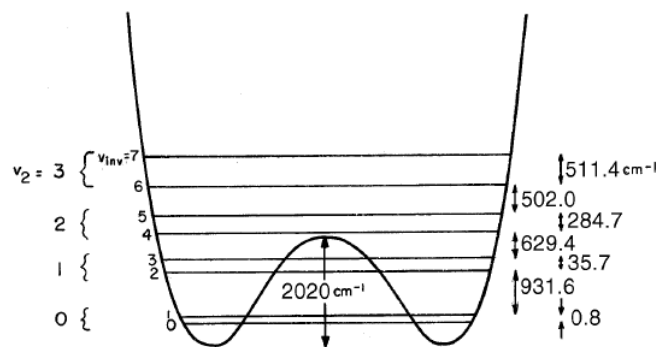
**S-T splitting**

**Dihydrides:**



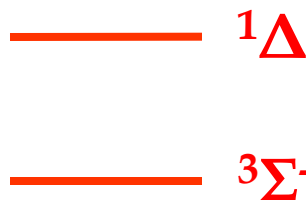
**Renner Effect**

**Trihydrides:**



**Inversion tunneling**

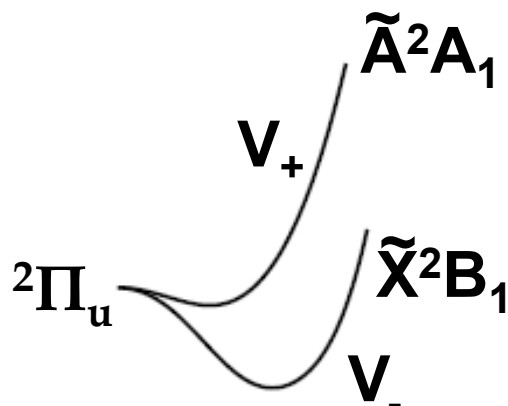
Monohydrides:



S-T splitting

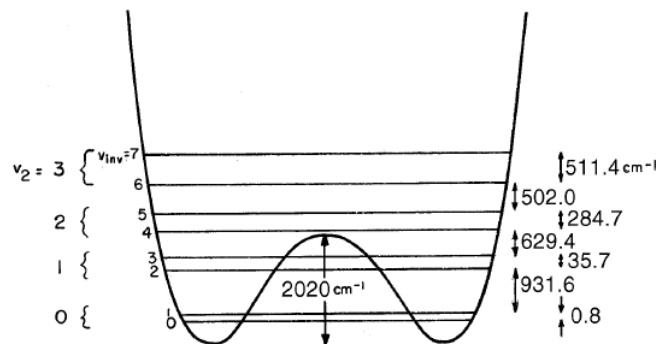
**SbH<sub>2</sub>:**

CAS-SCF MRCI  
 124 geometries



Renner Effect

Trihydrides:



Inversion tunneling

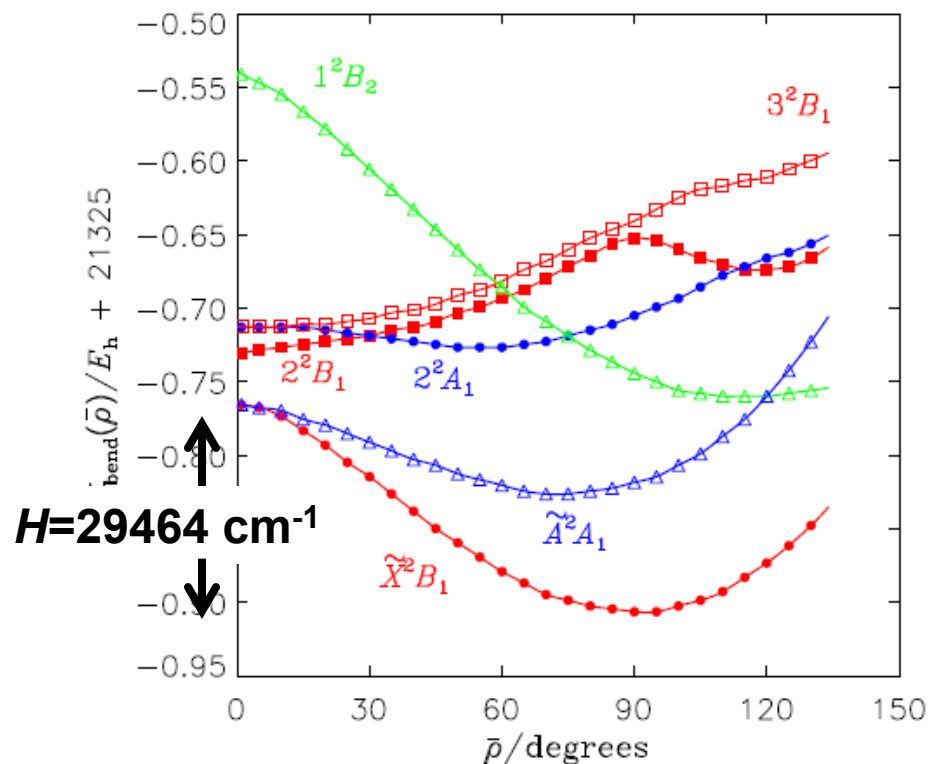
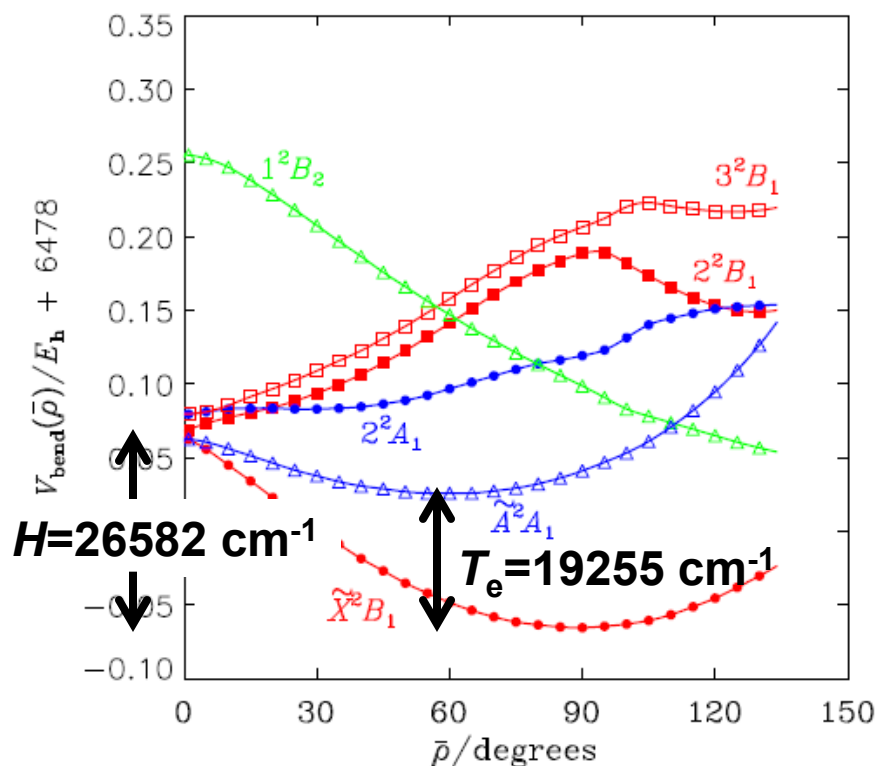
## SbH<sub>2</sub> Bending Potential Curves

$$R_e = 1.719 \text{ \AA}$$

Using CAS-SCF MRCI for full surfaces

## BiH<sub>2</sub> Bending Potential Curves

$$R_e = 1.803 \text{ \AA}$$



$H = 26470 \text{ cm}^{-1}$   $T_e = 19478 \text{ cm}^{-1}$  ← CCSD(T) a better ab initio method

# Ab initio slide: $\text{SbH}_2$

(no talk should be without one)

- all-electron complete active space self-consistent field (CASSCF) method, followed by a multireference
- configuration interaction (MRCI) treatment
- Hydrogen: aug-cc-pV5Z basis set
- Antimony: Sapporo-DKH3-QZP-2012 basis set
- non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonians

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

(using Breit-Pauli operator)

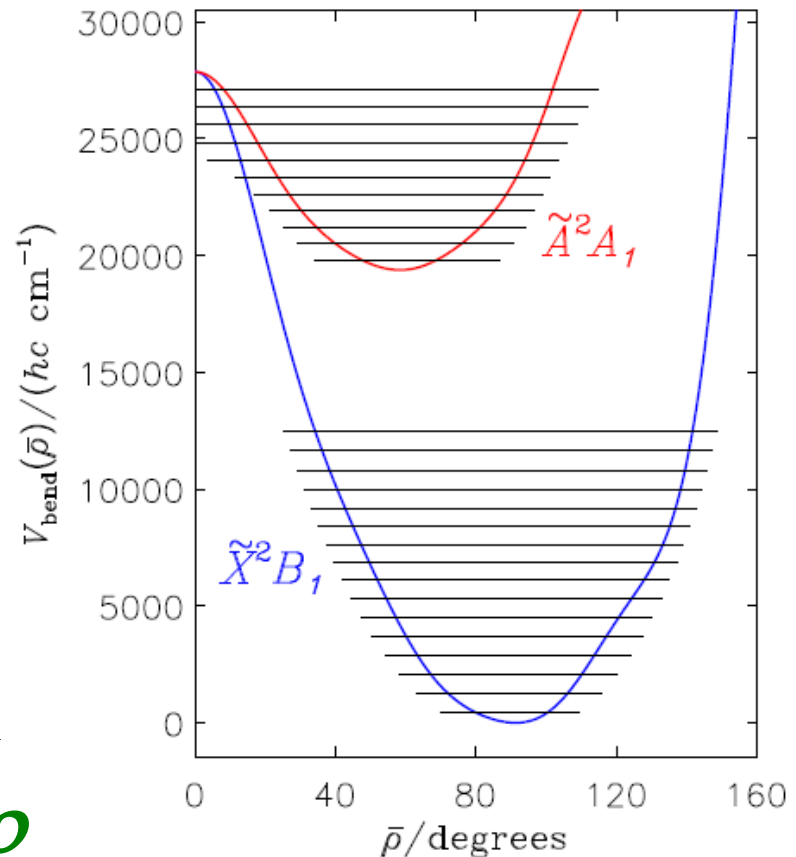
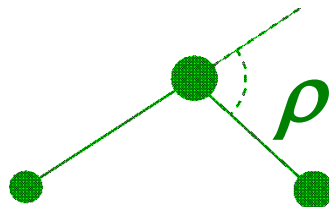


Table 3: Calculated rovibronic term values (in  $\text{cm}^{-1}$ ) for selected  $(v_1, v_2, v_3)$  states  $\bar{X}^2B_1$   $^{121}\text{SbH}_2$ .

$N_{K_a K_c}$ $(v_1, v_2, v_3)$	$0_{00}$		$1_{01}$		$1_{11}$		$1_{10}$	
	$F_1^a$		$F_2^a$	$F_1^a$	$F_2$	$F_1$	$F_2$	$F_1$
(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

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

Local Mode  
behaviour



Rovibronic  
Level  
Clustering  
At high  $J$



## Simulation of $\text{SbH}_2$ absorption spectrum, 0 to 5000 $\text{cm}^{-1}$

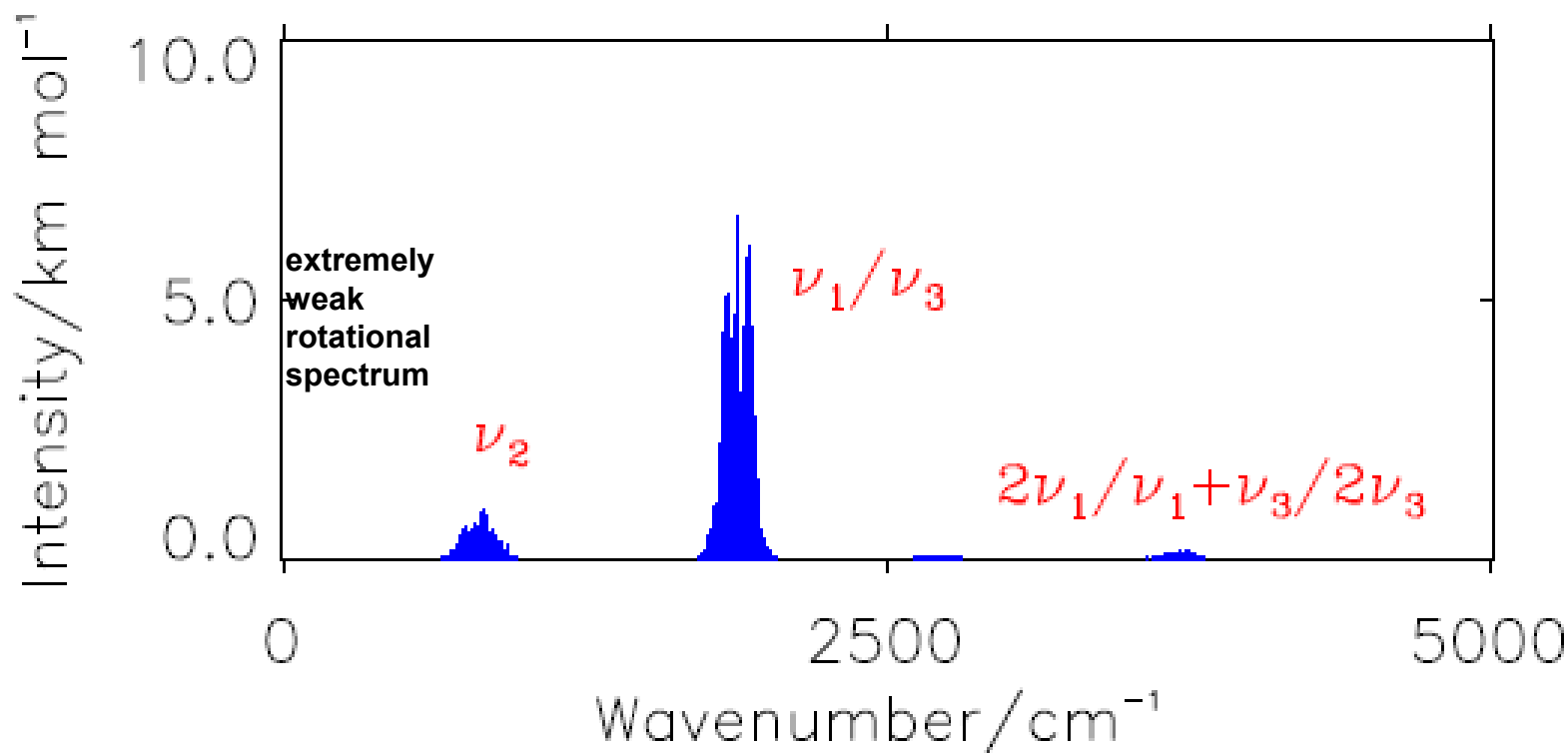


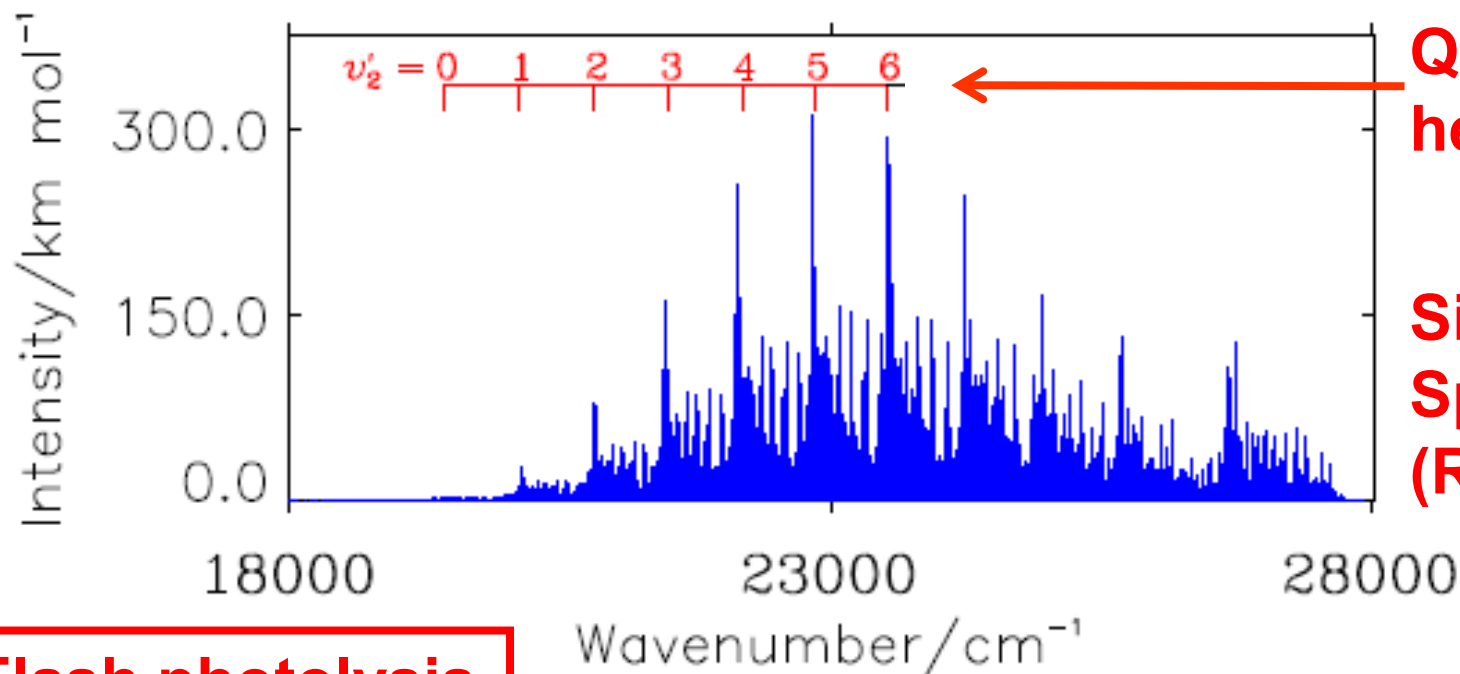
Figure 4: The infrared absorption spectrum of  $\tilde{X}^2B_1$   $^{121}\text{SbH}_2$  and  $^{123}\text{SbH}_2$  in natural abundance, simulated at a temperature of  $T = 300$  K. States with  $J \leq 19/2$  are taken into account.

## Experiments:

- 1. Matrix isolation infrared spectrum obtained by reacting laser ablated Sb with hydrogen.**  
**Wang, Souter and Andrews, JPCA, 107, 4244 (2003)**
- 2. The visible absorption spectrum obtained by flash photolysis of stibine ( $\text{SbH}_3$ ).**  
**Basco and Lee, Spectrosc. Lett. 1, 13 (1968)**
- 3. The visible emission spectrum obtained by UV laser photolysis of stibine.**  
**Ni, Yu, Ma and Kong, CPL 128, 270 (1986)**



## Visible absorption spectrum of $\text{SbH}_2$



**Flash photolysis**

Figure 5: The  $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$  electronic absorption spectrum of  $^{121}\text{SbH}_2$  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. 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,

## IR spectrum of **Laser ablated Sb + H<sub>2</sub> → matrix isolation**

Table 7: Stretching fundamental term values for  $\tilde{X}^2B_1$  SbH<sub>2</sub>, SbD<sub>2</sub>, and SbHD: Experimental values determined by Wang *et al.* [19] compared to values calculated in the present work.

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

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

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  $^{121}\text{SbH}_2$ .

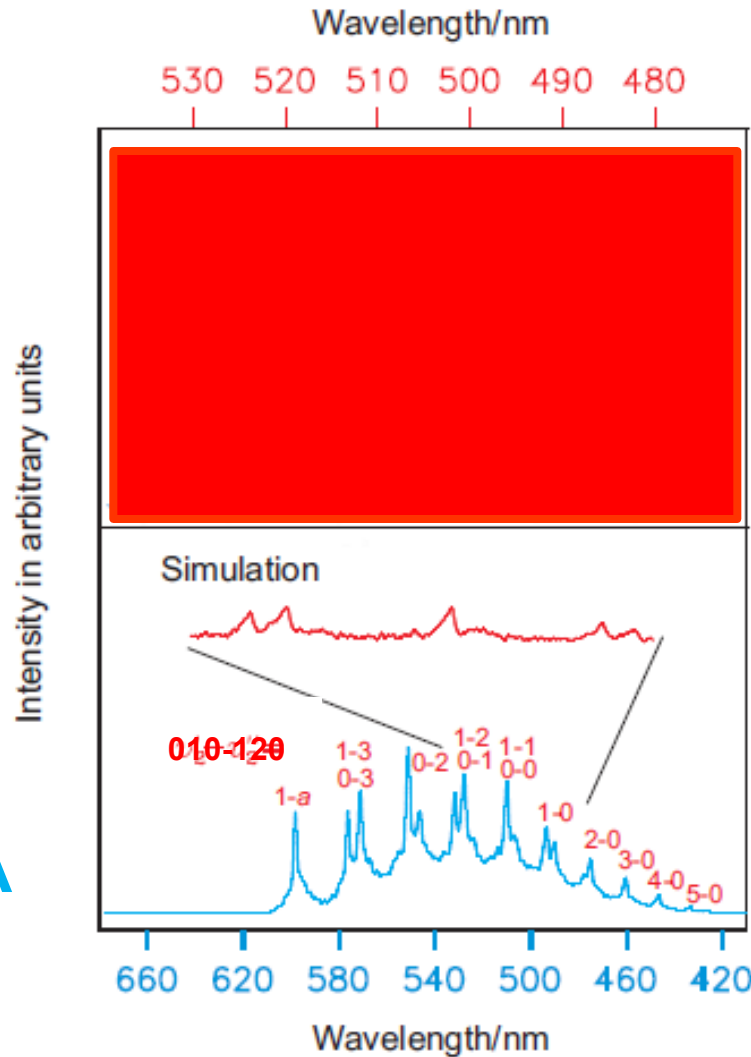
$(v_2')^a$	$\tilde{\nu}_{\text{obs}}$	$\tilde{\nu}_{\text{calc}}^b$	O-C <sup>c</sup>
0	19438	19459.8	-22
1	20131	20156.4	-25
2	20822	20827.7	-6
3	21511	21480.6	30
4	22191	22147.1	44
5	22863	22843.6	19
6	23529	23539.8	-11
7		24244.3	
8		24961.5	
9		25675.1	
10		26669.9	

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

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

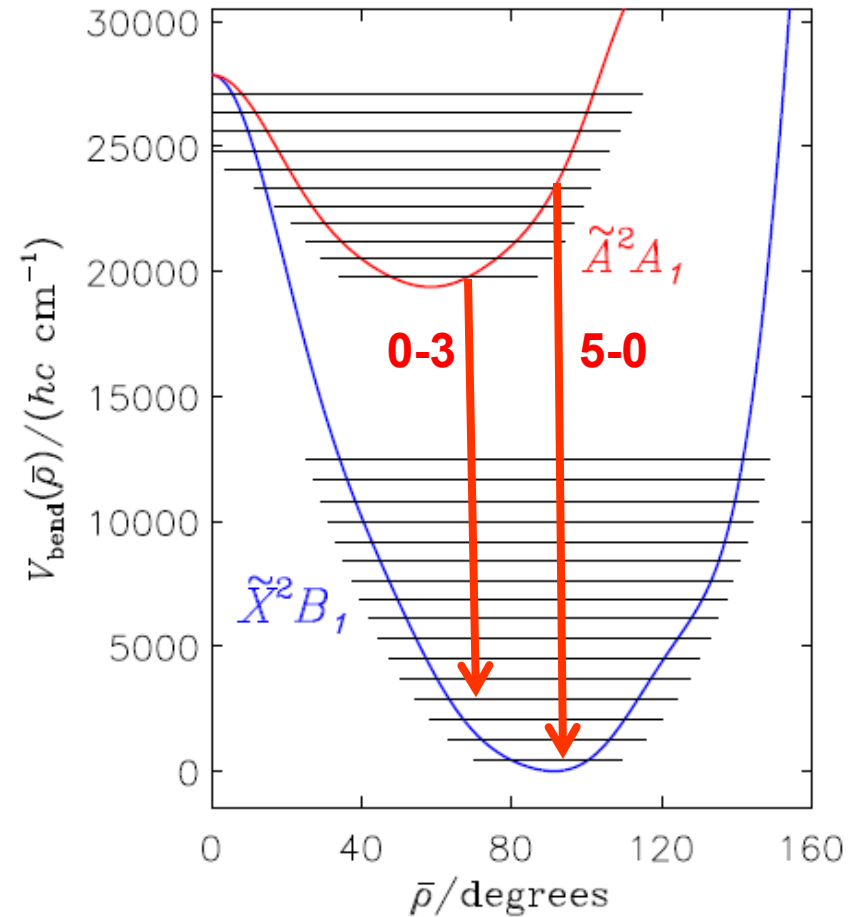
It's what you call  
"fortuitous"

# Emission spectrum. ArF laser photolysis of $\text{SbH}_3$



3 Å

12 Å



$$J(\text{max}) = 49/2$$

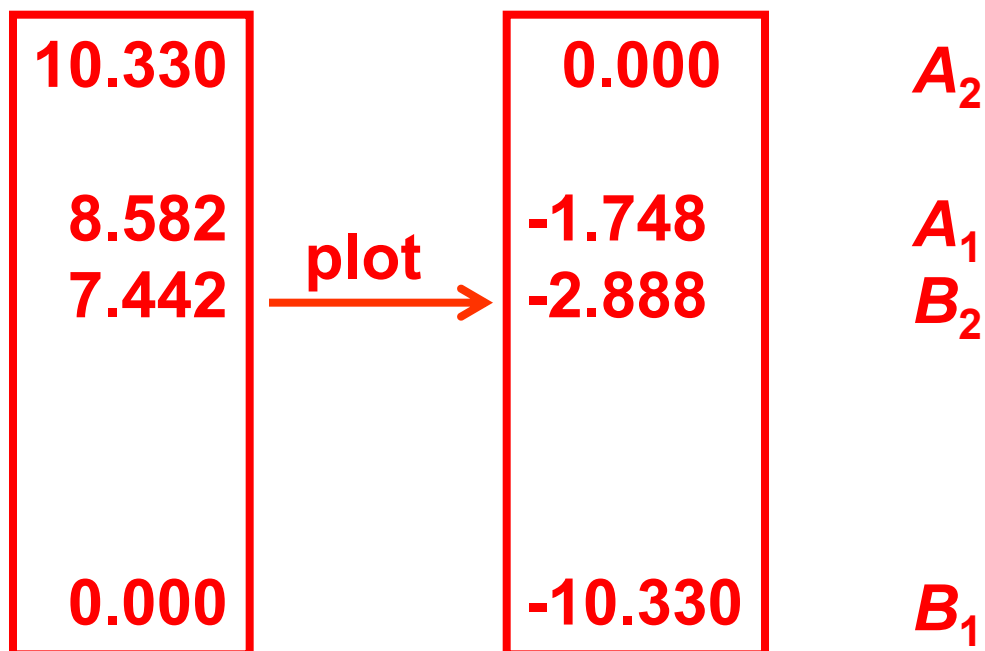
Simulation temperature = 1200 K for predominantly A-state levels.

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

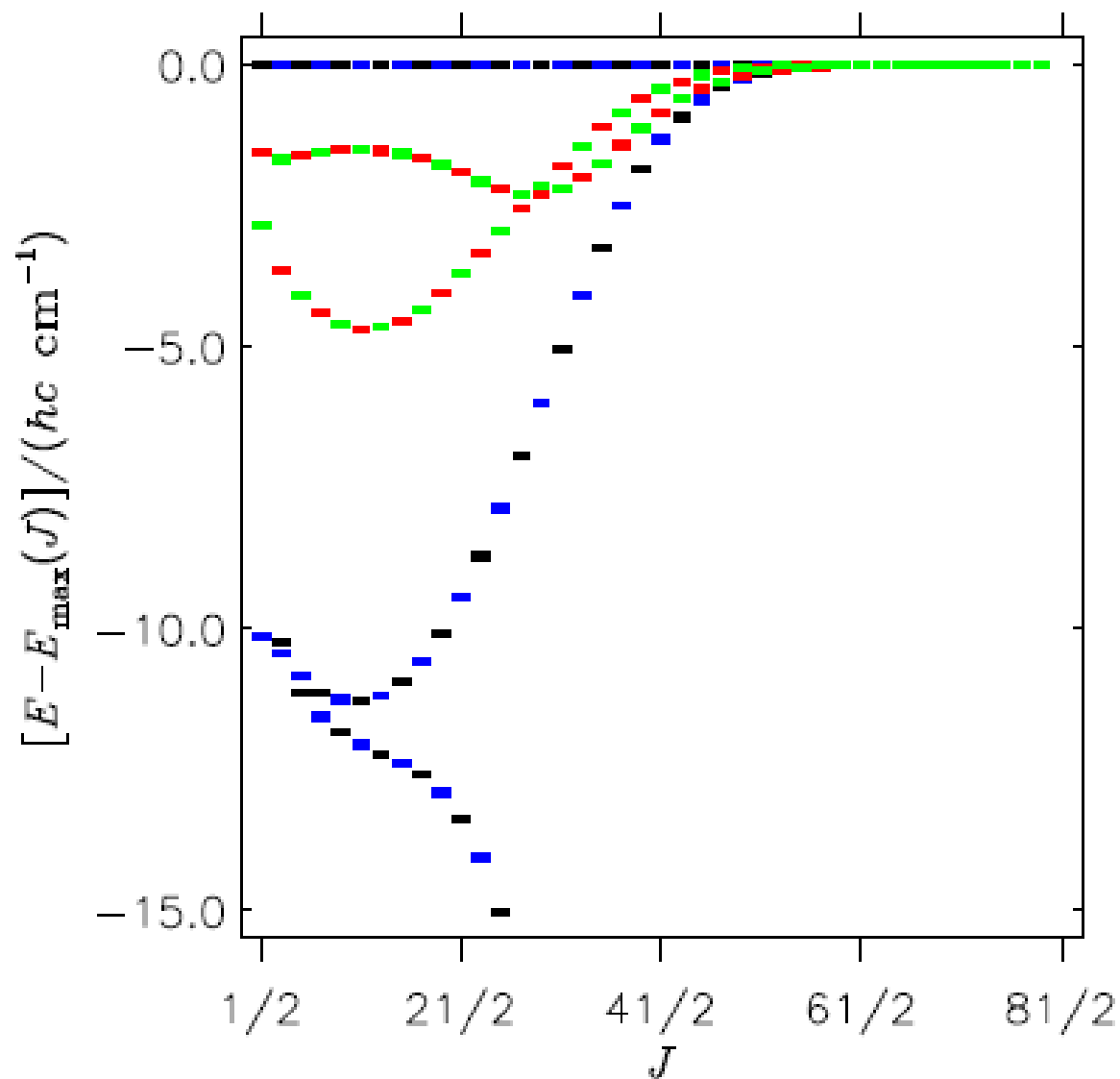
$N_{K_a K_c}$	$0_{00}$	$1_{01}$		$1_{11}$		$1_{10}$	
$(v_1, v_2, v_3)$	$F_1^a$	$F_2^a$	$F_1^a$	$F_2$	$F_1$	$F_2$	$F_1$
$(0,0,0)$	0.000	8.582	8.656	7.442	9.318	10.330	12.174

$J = 1/2$  term values

Rovibronic symmetry



## Rovibronic energy level clustering at very high $J$ -values



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