An *ab initio* study of SbH_2 and BiH_2: The Renner Effect, Spin-Orbit Coupling, Local Mode Vibrations and Rovibronic Energy Level Clustering in SbH_2

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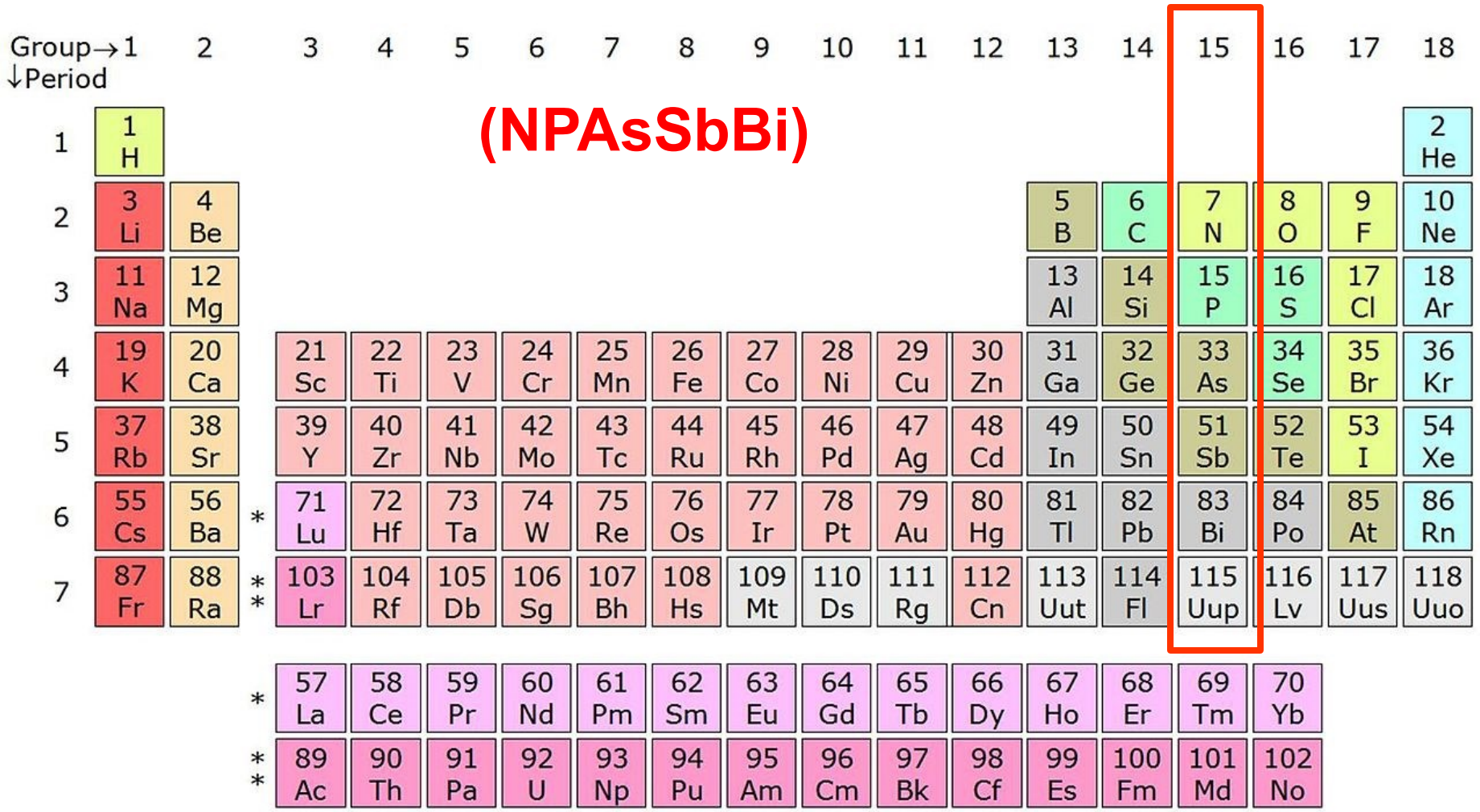
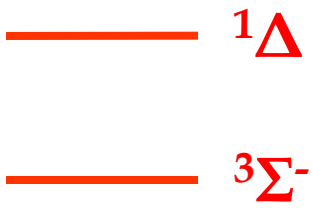
The Group 15 (PNICTOGEN) Hydrides



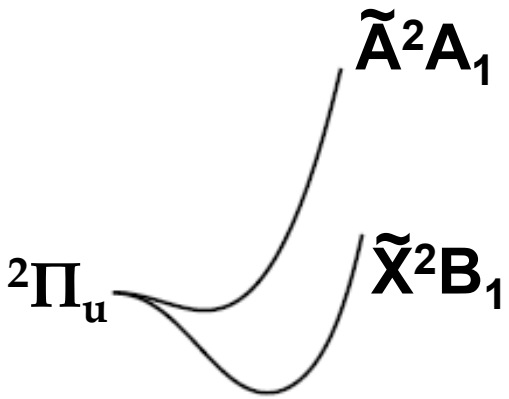
The Group 15 (N-P-As-Sb-Bi) Hydrides

Monohydrides:



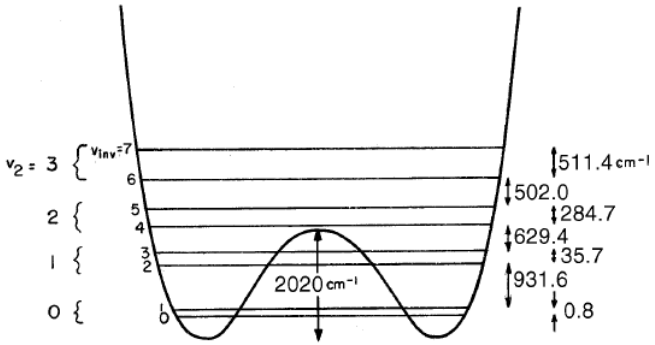
S-T splitting

Dihydrides:



Renner Effect

Trihydrides:



Inversion tunneling

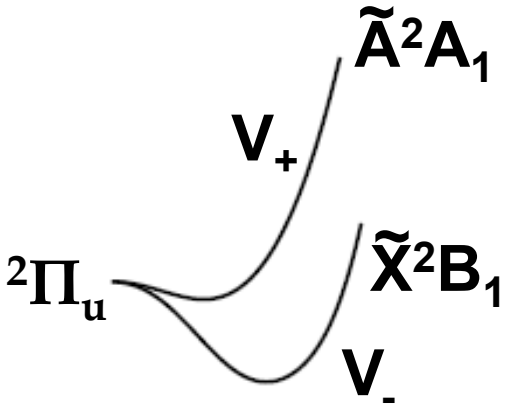
Monohydrides:

$^1\Delta$

$^3\Sigma^-$

S-T splitting

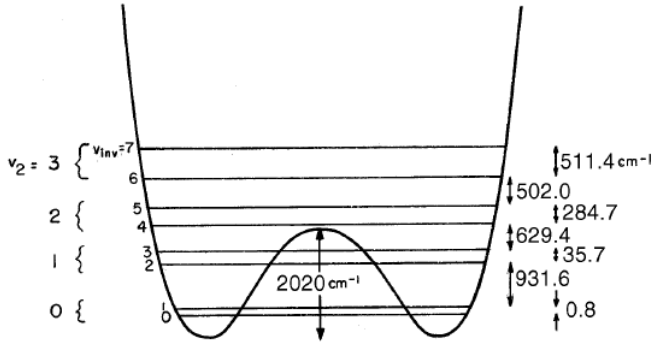
SbH_2:



Renner Effect

CAS-SCF MRCI
124 geometries

Trihydrides:



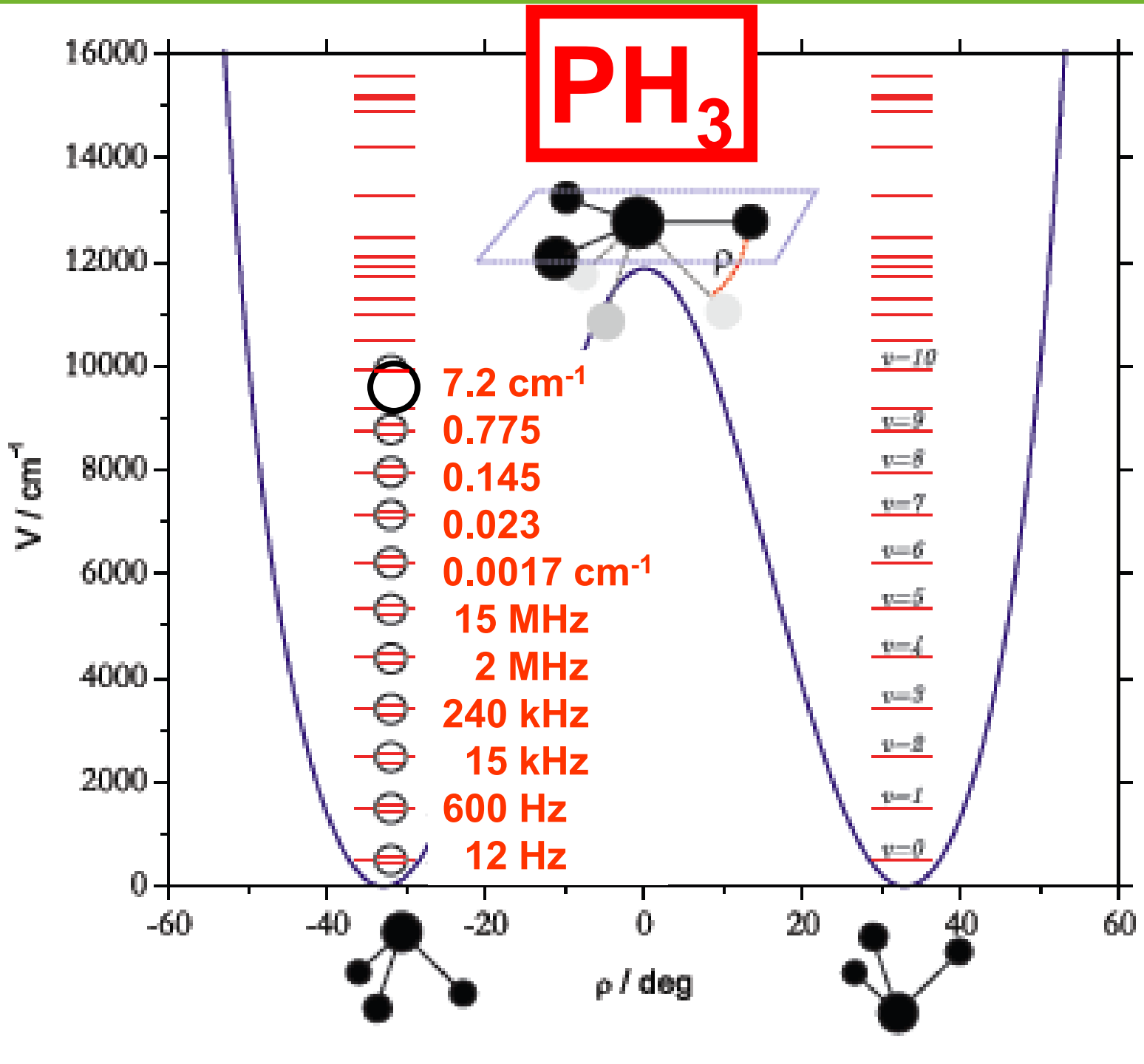
Inversion tunneling

THE PH_3 MOLECULE

Barrier height = 12300 cm^{-1}

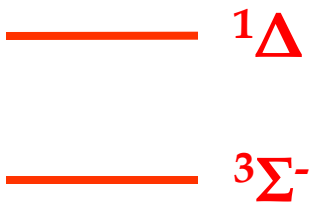
**Schwerdtfeger, Laakkonen and Pekka Pyykkö,
J. Chem. Phys., 96, 6807 (1992)**

**Recent theoretical calcs by
Sousa-Silva, Polyanski, Yurchenko and Tennyson
From UCL, UK.
Yield the tunneling splittings given on the next slide**


PH3
16000
14000
12000
10000
8000
6000
4000
2000
0
V / cm-1
-60
-40
-20
0
20
40
60
ρ / deg
ρ
v=10
v=9
v=8
v=7
v=6
v=5
v=4
v=3
v=2
v=1
v=0
7.2 cm-1
0.775
0.145
0.023
0.0017 cm-1
15 MHz
2 MHz
240 kHz
15 kHz
600 Hz
12 Hz

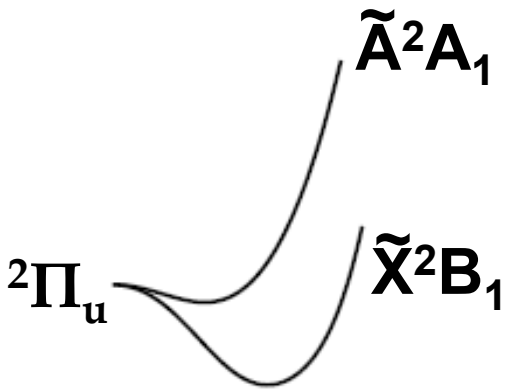
The Group 15 (N-P-As-Sb-Bi) Hydrides

Monohydrides:



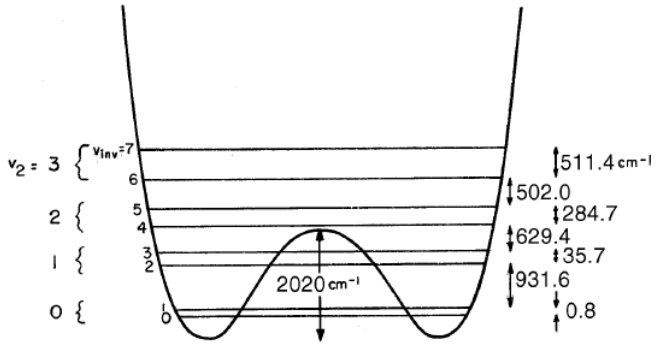
S-T splitting

Dihydrides:



Renner Effect

Trihydrides:



Inversion tunneling

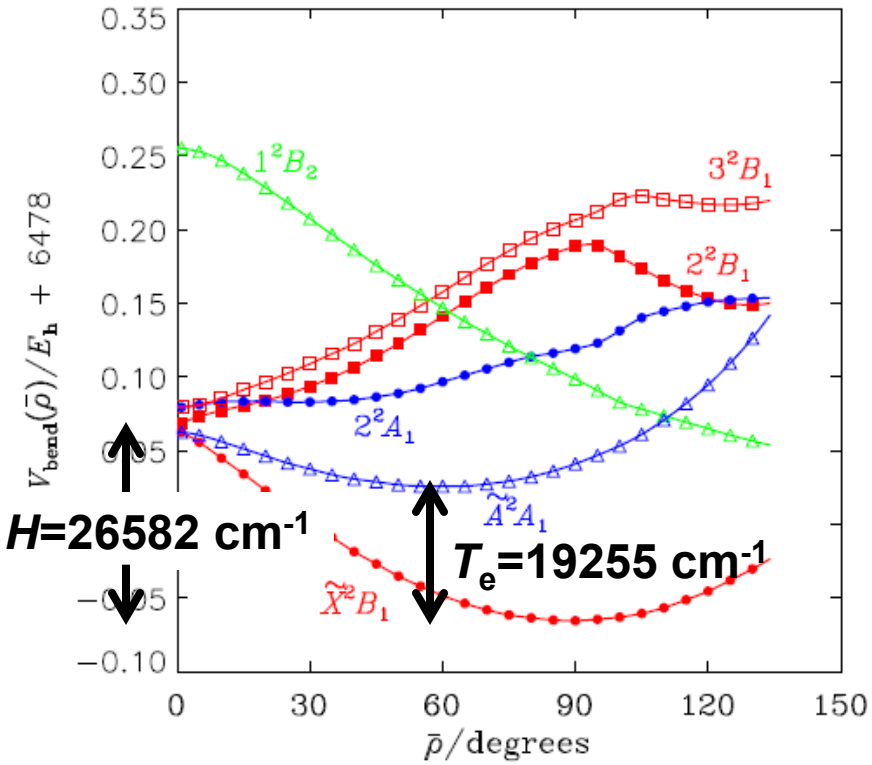
SbH_2 Bending Potential Curves

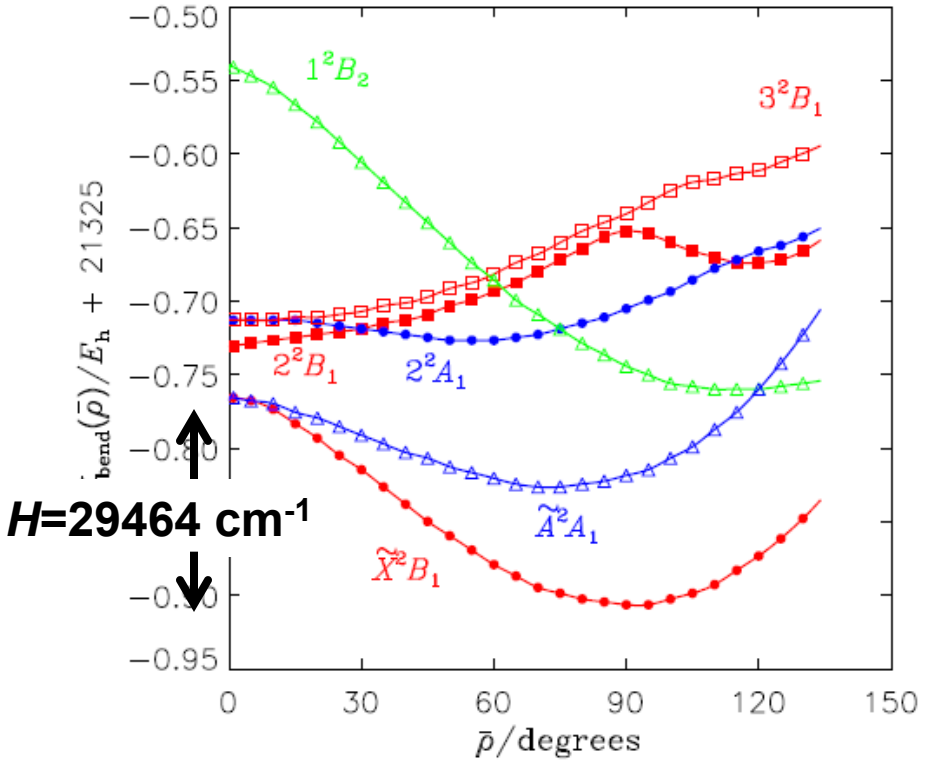
R_e = 1.719Å

BiH_2 Bending Potential Curves

R_e = 1.803Å

Using CAS-SCF MRCI for full surfaces



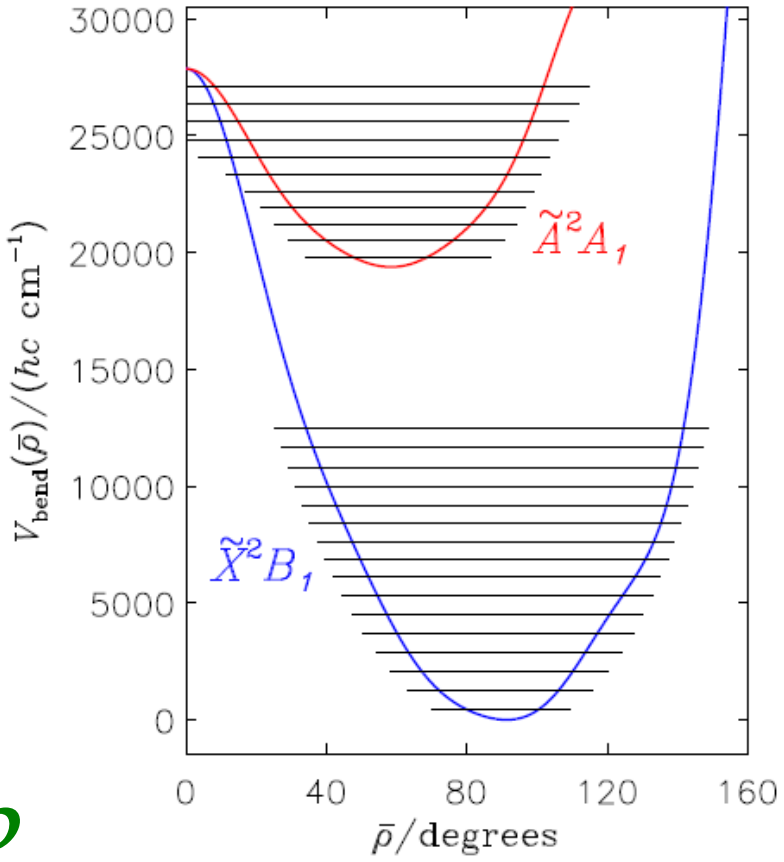


H=26470 cm^{-1} T_e=19478 cm^{-1} ← CCSD(T) a better ab initio method

Ab initio slide: SbH_2

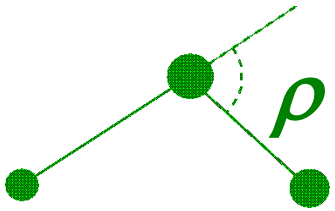
(no talk should be without one)

- 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



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

(using Breit-Pauli operator)



Local Mode behaviour

Rovibronic Level Clustering At high *J*

Table 3: Calculated rovibronic term values (in cm^{-1}) for selected (v_1, v_2, v_3) states $\tilde{X}^2B_1$ $^{121}SbH_2$.

$N_{K_aK_c}$	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
(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

[a]An F_2 state has $J = N - 1/2$; an F_1 state has $J = N + 1/2$.

Simulation of SbH_2 absorption spectrum, 0 to 5000 cm^{-1}

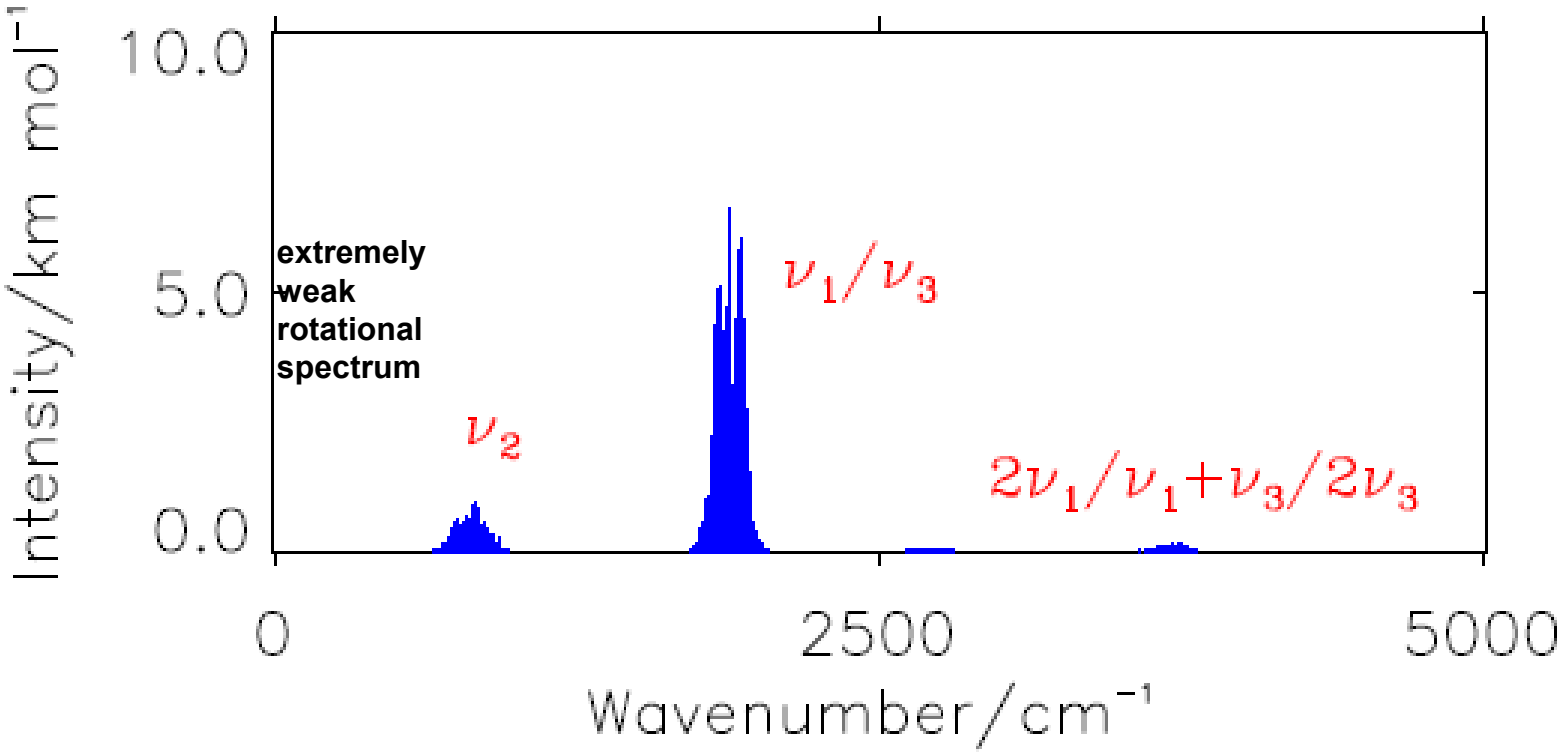


Figure 4: The infrared absorption spectrum of $\tilde{X}^2B_1$ $^{121}SbH_2$ and $^{123}SbH_2$ in natural abundance, simulated at a temperature of $T = 300$ K. States with $J \leq 19/2$ are taken into account.

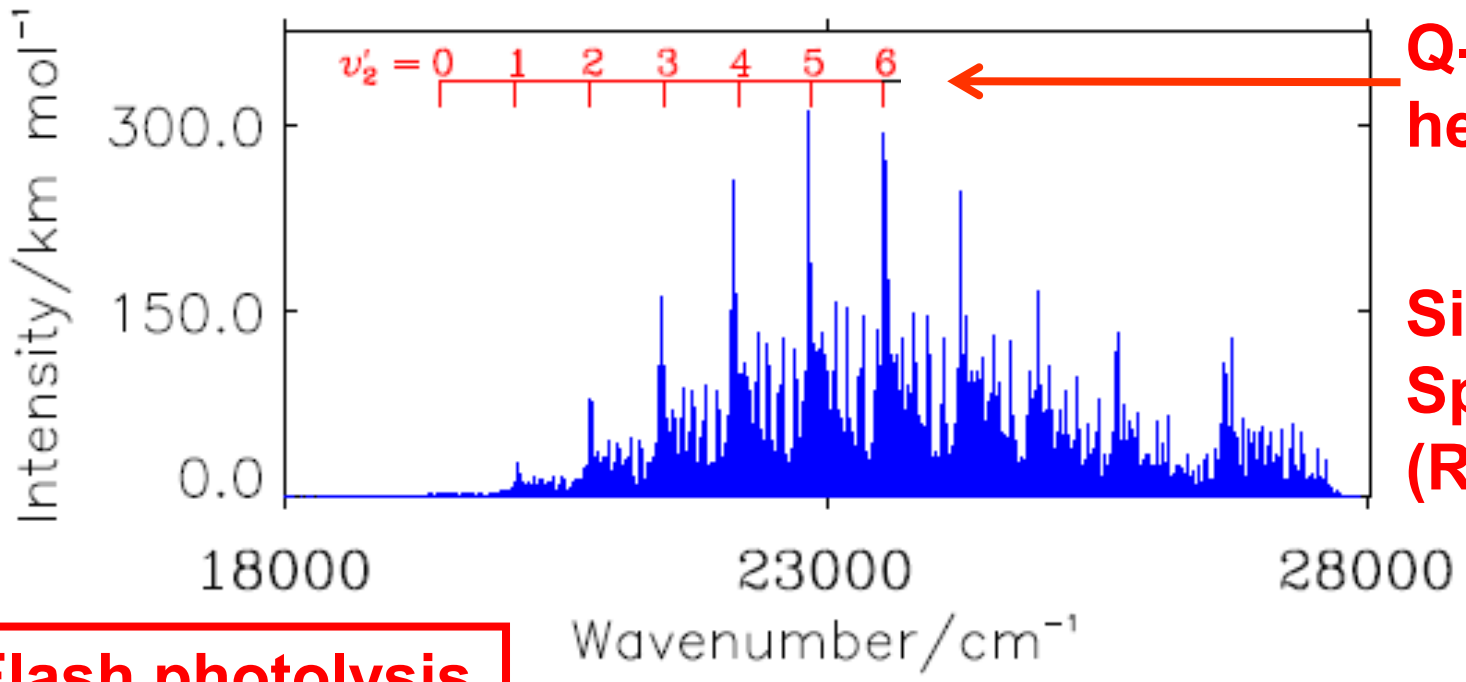
Experiments:

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 (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 SbH_2



Measured Q-branch heads

Simulated Spectrum (RENNER)

Flash photolysis

Figure 5: The $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$ electronic absorption spectrum of $^{121}SbH_2$ and $^{123}SbH_2$ 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 $\tilde{A}(0, v_2', 0) \leftarrow \tilde{X}(0, 0, 0)$ ($v_2' = 0, 1, \ldots, 6$; see Table 8) are indicated by the red part of the wavenumber comb,

IR spectrum of Laser ablated Sb + H_2 → matrix isolation

Table 7: Stretching fundamental term values for $\tilde{X}\,^2B_1$ SbH_2, SbD_2, and SbHD: Experimental values determined by Wang *et al.* [19] compared to values calculated in the present work.

Molecule	Environment	ν_1/cm^{-1}	ν_3/cm^{-1}
SbH_2	pure H_2	1869.7	1878
	Ne/H_2	1879.0	1883.9
	Ar/H_2	1863.7	1869.0
$^{121}SbH_2$	Calc.[a]	1876.0	1873.4
SbD_2	pure D_2	1341.9	1345.8
	Ne/D_2	1349.4	1352.0
	Ar/D_2	1337.6	1341.8
$^{121}SbD_2$	Calc.[b]	1342.7	1340.5
SbHD	Ar/HD	1339.6	1866.5
^{121}SbHD	Calc.[c]	1341.9	1874.0

Experiment has $\nu_3 > \nu_1$ from NH_2

Table 8: Experimentally observed Q-head positions $\tilde{\nu}_{\mathrm{obs}}$ (cm^{-1}) in the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$ absorption spectrum of SbH_2 [20] compared to vibronic energy spacings $\tilde{\nu}_{\mathrm{calc}}$ (cm^{-1}) of $^{121}SbH_2$.

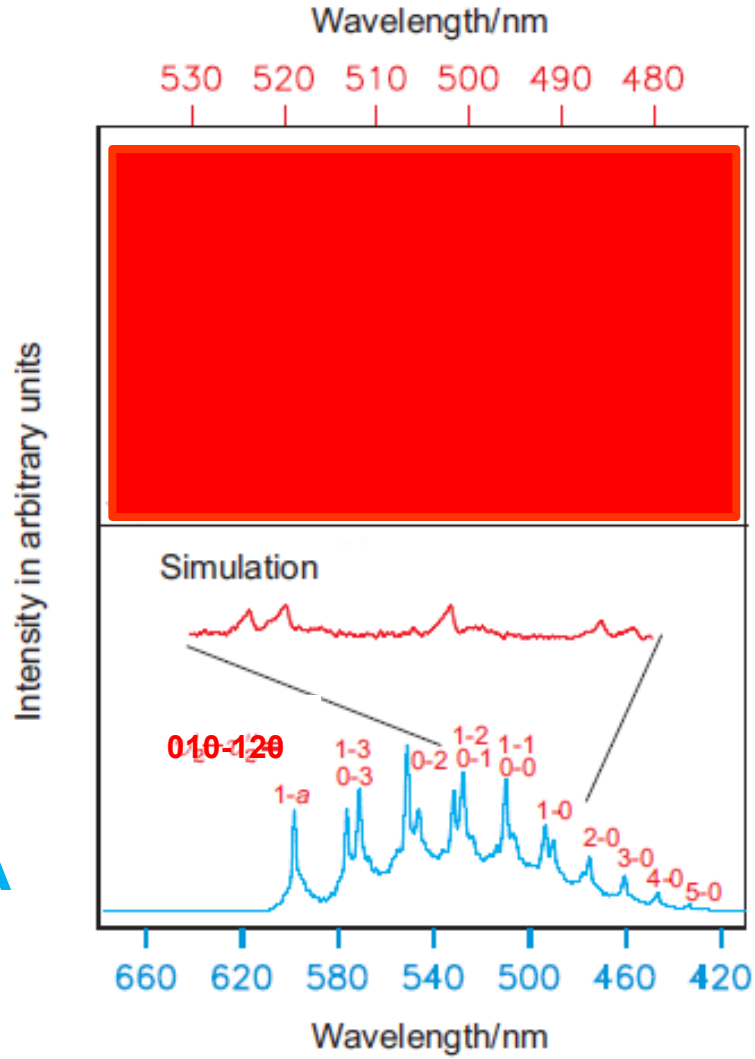
$(v_2')^a$	$\tilde{\nu}_{\mathrm{obs}}$	$\tilde{\nu}_{\mathrm{calc}}{}^b$	O−C^c
0	19438	19459.8	−22
1	20131	20156.4	−25
2	20822	20827.7	−6
3	21511	21480.6	30
4	22191	22147.1	44
5	22863	22843.6	19
6	23529	23539.8	−11
7		24244.3	
8		24961.5	
9		25675.1	
10		26669.9	

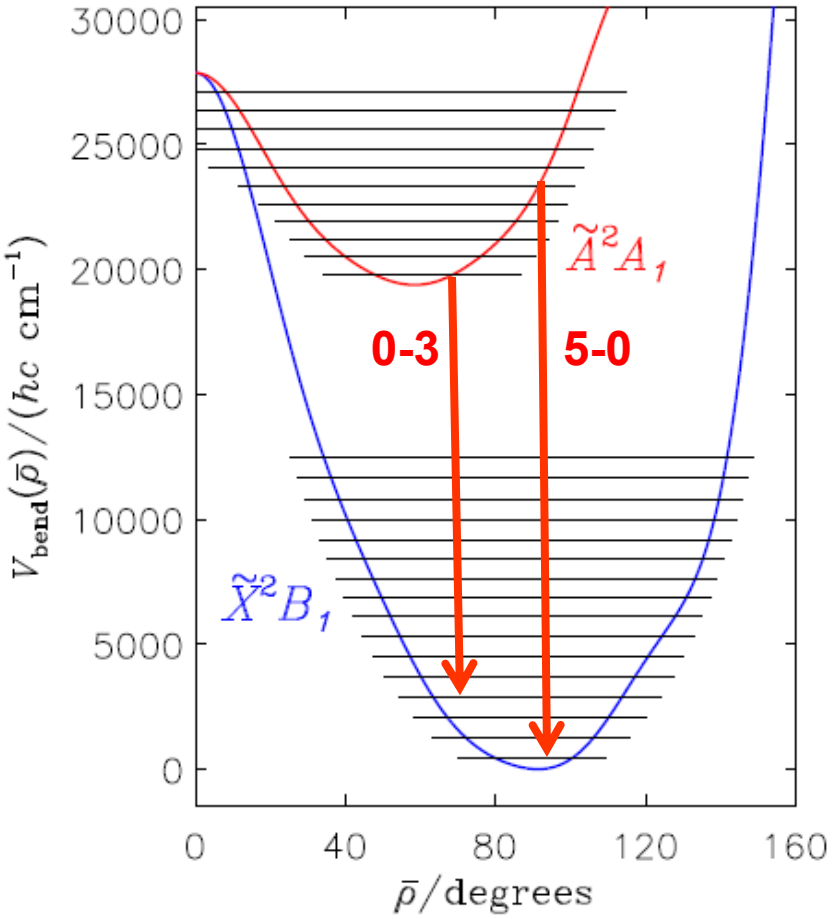
BUT T_e **(CAS-SCF MRCI) = 19255 cm^{-1}**

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

It's what you call "fortuitous"

Emission spectrum. ArF laser photolysis of SbH_3





J(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

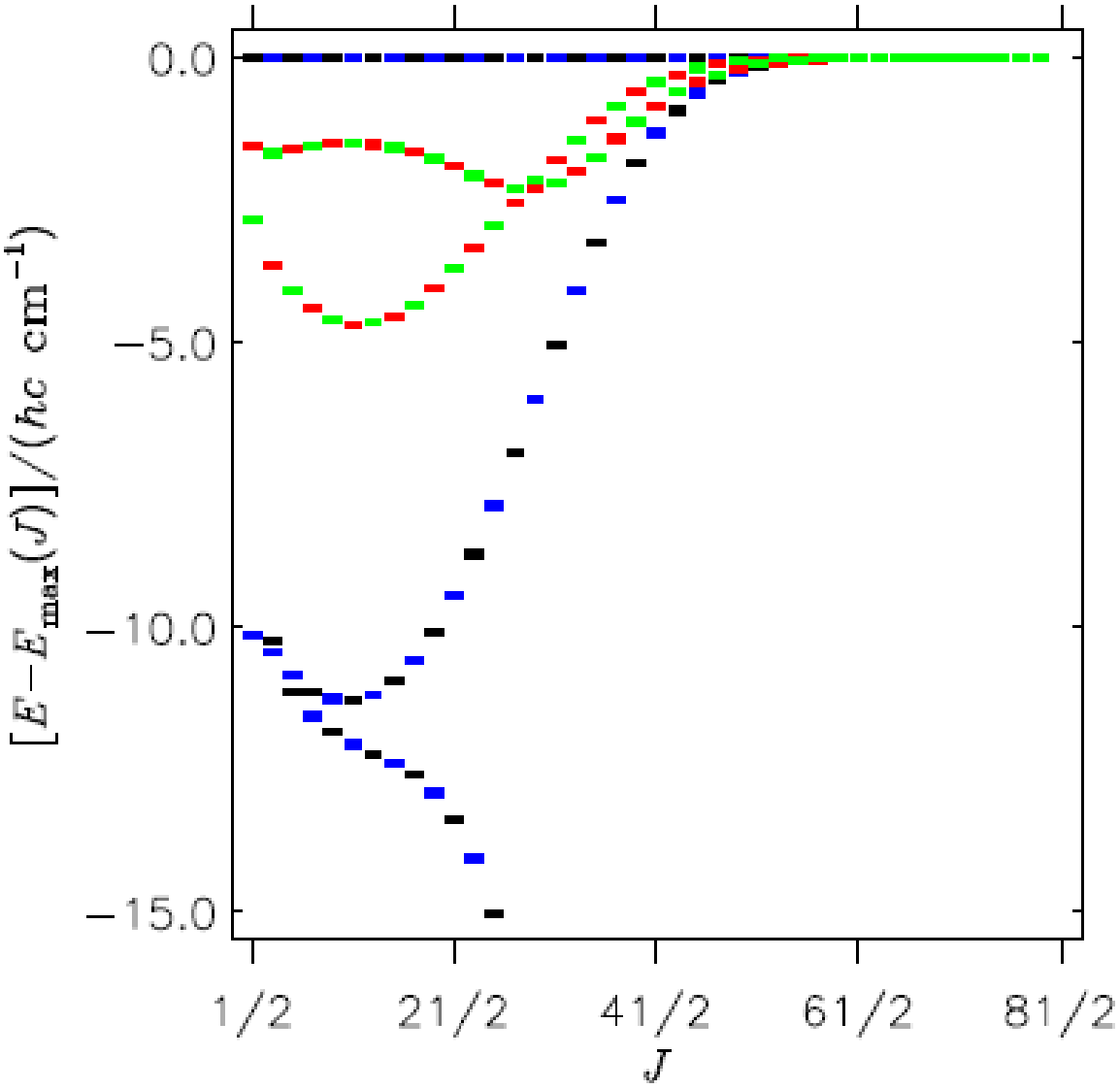
$N_{K_aK_c}$	0_{00}	1_{01}		1_{11}		1_{10}	
(v_1, v_2, v_3)	$F_1{}^a$	$F_2{}^a$	$F_1{}^a$	F_2	F_1	F_2	F_1
(0,0,0)	0.000	8.582	8.656	7.442	9.318	10.330	12.174

$J = ½$ term values

Rovibronic symmetry

10.330		0.000	A_2
8.582	plot →	-1.748	A_1
7.442		-2.888	B_2
0.000		-10.330	B_1

Rovibronic energy level clustering at very high *J*-values



Red A_1

Black A_2

Blue B_1

Green B_2

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Umpei Nagashima
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Roman I. Ovsyannikov
Peter Schwerdtfeger
Walter Thiel
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