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And now for something completely different...



(Picture courtesy of M. Python)

Theoretical rovibronic energies of pathological molecules: Extreme flexibility and Born-Oppenheimer breakdown

1

Per Jensen

School of Mathematics and Natural Sciences Physical and Theoretical Chemistry University of Wuppertal D-42097 Wuppertal Germany

> Tel. +49 (0) 202 - 439 2468 jensen@uni-wuppertal.de



Rovibrational motion in cold molecules: Example: dimethyl ether



Motion in cold molecules

- Born-Oppenheimer approximation (Electronic ground state)
- Overall rotations
- Small amplitude vibrations
- Large amplitude vibrations (e.g., internal rotations)

Starting point for theoretical description: **Separate** treatment of the different motions

$$\begin{aligned} \widehat{H}_{\text{full}} &= \widehat{H}_{\text{rot}} + \ \widehat{H}_{\text{LAV}} + \widehat{H}_{\text{SAV}} \\ |\psi_{\text{full}}\rangle &= |\psi_{\text{rot}}\rangle |\psi_{\text{LAV}}\rangle |\psi_{\text{SAV}}\rangle \end{aligned}$$

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Protonated methane CH₅⁺



Beyond rotation-vibration separation: Extremely flexible protonated methane

4

"I anticipate that this enfant terrible will be caught in interstellar space far ahead of its theoretical understanding which will take at least a few more decades." [1]



Motion in CH₅⁺

- Five protons but four bonds
- No well-defined, static equilibrium geometry
- Internal rotations & flips
- ⇒ Rotation and vibration inseparable [2]

 $\hat{H}_{\text{full}} = \hat{H}_{\text{rot}} + \hat{H}_{\text{LAV}} + \hat{H}_{\text{SAV}}$ $|\psi_{\text{full}}\rangle = |\psi_{\text{rot}}\rangle |\psi_{\text{LAV}}\rangle |\psi_{\text{SAV}}\rangle$

First observation: Free internal rotation angle and axis!

^[1] Oka, T.; Science 347, 1313 (2015); Animation: http://www.theochem.ruhr-uni-bochum.de/go/ch5p.html (D. Marx)
[2] Schmiedt, H., et al.; J. Chem. Phys. 143, 154302 (2015)



Free internal rotation axis and angle: The potential energy surface



5

- 120 equivalent minima
- Zero point energy comparable to all barriers!

Our starting point: Completely flat potential

^[3] Structures and barriers from: Bunker, P.R., et al.; J. Mol. Struc. 695-696, (2003)



Pedagogical example for better understanding: Rigid methane

- Non-vibrating, static methane molecule = rigid spherical top
- Hamiltonian: $\widehat{H} = B(\widehat{J}_x^2 + \widehat{J}_y^2 + \widehat{J}_z^2)$
- Full rotational symmetry: Group *K*(mol), isomorphic to SO(3)
- Irreducible representations D_J , J = 0, 1, 2, 3, 4, ...

 $E_J = B J(J+1)$

- Vibrating, actually existing methane molecule
- Molecular symmetry group $T_d(M) \subset SO(3)$



6

Labeled by irreducible representations of $T_{d}(M) \subset SO(3)$

P. R. Bunker and P. Jensen: Spherical Top Molecules and the Molecular Symmetry Group, Mol. Phys. 97, 255-264 (1999).



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Pedagogical example continued: Protonated methane simplified

7

- Protonated methane with two "soft" vibrations
- Now five-dimensional rotor [4]: $\hat{H} = \frac{B}{2} \sum_{a < b} \hat{J}_{ab}^2$
- 5D rotational symmetry: Group SO(5)
- Irreducible representations $[n_1, n_2], n_1 \ge n_2 = 0, 1, 2, 3, 4, ...$

e e

 $E_{[n_1,n_2]} = \frac{B}{2} \{n_1(n_1+3) + n_2(n_2+1)\}$

- Fully vibrating, actually existing protonated methane molecule
- Molecular symmetry group $G_{240} \subset SO(5)$



Labeled by irreducible representations of $G_{240} \subset SO(5)$

[4] e.g.. Racah, G.; *Phys Rev.* 76, 1352, (1949)



Permutation/inversion symmetry in protonated methane

Five identical particles: Symmetry group $G_{240} = S_5 \times \{E, E^*\}$ $S_5=(E),(12),(123),(1234),(12345),...$

- Molecular states labelled by S_5 labels (Fermi-Dirac-allowed: A_2, G_2, H_2)
- What is the permutation symmetry of the generalized rotational states?
 - *S*₅ is "isomorphic" to subgroup of SO(5) Permutations can be "translated" to 5d-rotations
 - Non-zero potential = Splitting





Electric dipole moment selection rules in SO(5)

9

- Space-fixed components of dipole moment has symmetry A_1 in S_5
- Assumption: In SO(5) there are contributions from all [n₁, n₂] that image onto A₁ by forward correlation

 $\Gamma_{\mu} = [3,1] \oplus [3,3] \oplus [4,2] \oplus [4,3] \oplus \dots$

 $([n_1',n_2'] \otimes [n_1,n_2]) \downarrow S_5 \supset A_1$

$\Gamma_{init}/\Gamma_{final}$	[0,0]	[1,0]	[1,1]	[2,0]	[2,1]	[2,2]
[0,0]	×	×	×	×	×	×
[1,0]	×	×	×	×	\checkmark	×
[1,1]	×	×	×	\checkmark	\checkmark	\checkmark
[2,0]	×	×	\checkmark	\checkmark	\checkmark	\checkmark
[2, 1]	×	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
[2,2]	×	×	\checkmark	\checkmark	\checkmark	\checkmark



Molecular super-rotor: Algebraic theory re-invented

Developed theory has great similarity to the algebraic theory by lachello and co-workers^{*,**}

10

New element is the use of the near-symmetry group SO(5) as starting point

*F. Iachello, Algebraic methods for molecular rotation-vibration spectra, *Chem. Phys. Lett.* **78**, 581–585 (1981).
**F. Iachello, R.D. Levine, Algebraic theory of molecules, in: Topics in Physical Chemistry, Oxford University Press, 1995.



Rovibrational energies of CH₅⁺ from experiment: Combination differences



Ground vibrational levels



- Scan rovibrational transitions (infrared)
- Construct the differences of all transitions (Combination differences = CoDiffs)
- If two transitions share upper level, this CoDiff occurs regularly (many upper states!)
- ➡ Differences rebuild ground state energy levels [6]

[6] Asvany, O. et al.; Science, 347, 1346 (2015)



Direct comparison of theory and experiment

12



First assignment of any of these experimental data consistent in energy and symmetry!



Comparison to experiment II

Symmetry	Exp. CoDiffs	Present work	Assignment
S_5	$[cm^{-1}]$	$[cm^{-1}]$	SO(5)
G_2	26.47252	25.71	[1,0] - [3,0]
	30.26984	29.38	[1,0] - [3,1]
	36.35280	36.73	[1,0] - [3,2]
H_2	39.68499	40.41	[2,1] - [4,2]
	47.32219	-	-
	51.80126	51.42	[2,1] - [4,3]([5,0])
	55.17916**	55.10	[2,1] - [5,1]
H_2	8.38325*	7.35	[2,2] - [3,1]
	21.52476*	22.04	[2,2] - [4,0]
	24.83280*	25.7124	[2,2] - [3,3]

- Remember: SO(5) theory is zero-order approximation
- There are many more lines in both experiment and theoretical prediction
- Expectation: Actual potential energy surface lifts the degeneracy of the

 S_5 states

Even more lines

Numbers from: Asvany, O. et al.; *Science*, **347**, 1346 (2015) (*) And (**) have been identified in the CoDiff spectrum only recently (Brackertz, S; Diploma thesis; University of Cologne; 2016) SCHOOL OF MATHEMATICS AND NATURAL SCIENCES PHYSICAL AND THEORETICAL CHEMISTRY



Comparison with conventional QM calculations

X.-G. Wang, T. Carrington, Vibrational energy levels of CH₅⁺, *J. Chem. Phys.* **129** 234102, (2008)

X.-G. Wang, T. Carrington, Calculated rotation-bending energy levels of CH₅⁺ and a comparison with experiment, *J. Chem. Phys.* **144**, 204304 (2016).





Outlook

General super-rotor theory

- Higher-order approximation (non-rigid super-rotor)
- Application to more molecules: Clusters, H_5^+ , ...
- Explicit symmetry breaking Link to hindered internal rotation

15

- Comparison to other models

Protonated methane

- Include potential energy surface in 5D-model
- Higher order effects (non-rigid, non-spherical,...)
- More measurements



Dramatis personæ for CH_5^+



Hanno Schmiedt Principal doer

Ponderers (answer phone, pontificate...)





Stephan Schlemmer

Per Jensen

- H. Schmiedt, S. Schlemmer, and P. Jensen: Symmetry of extremely floppy molecules: Molecular states beyond rotation-vibration separation, *J. Chem. Phys.* **143**, 154302/1-8 (2015). **DOI:** *10.1063/1.4933001*
- H. Schmiedt, P. Jensen, and S. Schlemmer: Collective molecular superrotation: A model for extremely flexible molecules applied to protonated methane, *Phys. Rev. Lett.*, **117**, 223002/1-5 (2016). **DOI:** *10.1103/PhysRevLett.117.223002*
- H. Schmiedt, P. Jensen, and S. Schlemmer: Rotation-vibration motion of extremely flexible molecules The molecular superrotor, *Chem. Phys. Lett.* **672**, 34–46 (2017). **DOI:** *10.1016/j.cplett.2017.01.045* "Frontiers article" prepared by invitation.
- H. Schmiedt, P. Jensen, and S. Schlemmer: The role of angular momentum in the superrotor theory for rovibrational motion of extremely flexible molecules, *J. Mol. Spectrosc., in press.* **DOI:** *10.1016/j.jms.2017.06.002*

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The Renner Effect

or:

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Computer programs:

RENNER:

Triatomic molecule in Renner-degenerate states. Only one linear geometry considered.

P. Jensen, M. Brumm, W. P. Kraemer, and P. R. Bunker, J. Mol. Spectrosc. 171, 31-57 (1995). DOI: 10.1006/jmsp.1995.1101
M. Kolbuszewski, P. R. Bunker, W. P. Kraemer, G. Osmann, and P. Jensen, Mol. Phys. 88, 105-124 (1996). DOI: 10.1080/00268979650026622
G. Osmann, P. R. Bunker, P. Jensen, and W. P. Kraemer, Chem. Phys. 225, 33-54 (1997). DOI: 10.1016/S0301-0104(97)00173-0

DR (Double Renner):

Triatomic molecule in Renner-degenerate states. Two linear geometries considered.

T. E. Odaka, P. Jensen, and T. Hirano, *J. Mol. Structure* 795, 14-41 (2006). DOI: 10.1016/j.molstruc.2005.10.059
V. V. Melnikov, T. E. Odaka, P. Jensen, and T. Hirano, *J. Chem. Phys.* 128, 114316/1-10 (2008). DOI: 10.1063/1.2827490



Variational calculation:

Construct matrix representation of the total Hamiltonian in terms of suitable basis functions

- Morse-oscillator (or Morse-oscillator–like) functions for stretching motion.
- Numerical bending functions generated by Numerov-Cooley integration
- Coupled (rigid rotor)-(electron spin) basis functions for the rotation ($\widehat{N}+\widehat{S}=\widehat{J}$)

Diagonalize matrix numerically – however the matrix blocks will become very large What should we do?



Contract!

Ignore end-over-end rotation and calculate the eigenenergies and wavefunctions for a hypothetical molecule that rotates about the *a* axis only.

Use (a smaller number of) the resulting eigenfunctions as basis functions for the final problem, including end-over-end rotation.

Principle of the contraction in DR





Total rovibronic wavefunction:





Electronic, rotational, e-spin:

 $|a; N, J, S, K, M_J, p\rangle = \cos[\gamma_K(\tau)] |\phi_1\rangle |N, J, S, K, M_J, p\rangle$

23

+ $\sin[\gamma_K(\tau)]i|\phi_{\tilde{B}}\rangle|N, J, S, K, M_J, \delta_{0p}\rangle$,

 $|b; N, J, S, K, M_J, p\rangle = \cos[\gamma_K(\tau)]i|\phi_{\tilde{B}}\rangle|N, J, S, K, M_J, \delta_{0p}\rangle$

 $- \sin[\gamma_K(\tau)] |\phi_1\rangle |N, J, S, K, M_J, p\rangle,$



 $\gamma_K(\tau)$

results from prediagonalization of Renner interaction at given value of the bending angle



Rotation, e-spin:

Symmetrized, "parity basis" $|N, J, S, K, M_J, p\rangle = \frac{1}{\sqrt{2}} \left[|N, J, S, K, M_J\rangle + (-1)^{N+K+p} |N, J, S, -K, M_J\rangle \right]$

Unsymmetrized, coupled rotation/e-spin

$$N, J, S, k, M_J \rangle = \sum_{m=-N}^{N} \sum_{M_S=-S}^{S} (-1)^{N-S+M_J} \sqrt{2J+1}$$
$$\times \begin{pmatrix} N & S & J \\ m & M_S & -M_J \end{pmatrix} |S, M_S\rangle |N, k, m\rangle$$

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25

H=26470 cm⁻¹

 $T_{e}=19478 \text{ cm}^{-1} \leftarrow \text{CCSD}(T)$ a better ab initio method



Ab initio slide: SbH₂

26

(no talk should be without one)

- all-electron complete active space selfconsistent 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



(using Breit-Pauli operator)





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

Local Mode behaviour

NKaKc	000	10)1	11	1	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)	8966 489	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

Rovibronic Level Clustering At high J

^{*a*}An F_2 state has J = N - 1/2; an F_1 state has J = N + 1/2.



Simulation of SbH₂ absorption spectrum, 0 to 5000 cm⁻¹

28



Figure 4: The infrared absorption spectrum of $\tilde{X}^2 B_1$ ¹²¹SbH₂ and ¹²³SbH₂ in natural abundance, simulated at a temperature of T = 300 K. States with $J \leq 19/2$ are taken into account.



Experiments:

- Matrix isolation infrared spectrum obtained by reacting laser ablated Sb with hydrogen. Wang, Souter and Andrews, JPCA, 107, 4244 (2003)
- The visible absorption spectrum obtained by flash photolysis of stibine (SbH₃).
 Basco and Lee, Spectrosc. Lett. 1, 13 (1968)
- The visible emission spectrum obtained by UV laser photolysis of stibine. Ni, Yu, Ma and Kong, CPL 128, 270 (1986)



IR spectrum of

Laser ablated Sb + $H_2 \rightarrow$ matrix isolation

Table 7: Stretching fundamental term values for $\tilde{X}^2 B_1$ SbH₂, SbD₂, and SbHD: Experimental values determined by Wang *et al.* [19] compared to values calculated in the present work.

Molecule	Environment	$\nu_1/{ m cm}^{-1}$	$ u_3/{ m cm}^{-1}$
SbH_2	pure H_2	1869.7	1878
	Ne/H_2	1879.0	1883.9
	$\rm Ar/H_2$	1863.7	1869.0
$^{121}SbH_2$	$\operatorname{Calc.}^{a}$	1876.0	1873.4
SbD_2	pure D_2	1341.9	1345.8
	$\rm Ne/D_2$	1349.4	1352.0
	$\rm Ar/D_2$	1337.6	1341.8
$^{121}\mathrm{SbD}_2$	$\operatorname{Calc.}^{b}$	1342.7	1340.5
SbHD	Ar/HD	1339.6	1866.5
$^{121}\mathrm{SbHD}$	$\operatorname{Calc.}^{c}$	1341.9	1874.0

Experiment has $\nu_3 > \nu_1$ from NH₂





Figure 5: The $\tilde{A}^2 A_1 \leftarrow \tilde{X}^2 B_1$ electronic absorption spectrum of ¹²¹SbH₂ and ¹²³SbH₂ 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 $\tilde{A}(0, v'_2, 0) \leftarrow \tilde{X}(0, 0, 0)$ ($v'_2 = 0, 1, ..., 6$; see Table 8) are indicated by the red part of the wavenumber comb,



Table 8: Experimentally observed Q-head positions $\tilde{\nu}_{obs}$ (cm⁻¹) in the $\tilde{A}^2 A_1 \leftarrow \tilde{X}^2 B_1$ absorption spectrum of SbH₂ [20] compared to vibronic energy spacings $\tilde{\nu}_{calc}$ (cm⁻¹) of ¹²¹SbH₂.

$(v_2')^a$	$\tilde{\nu}_{\rm obs}$	$\tilde{\nu}_{\rm calc}{}^{b}$	$O-C^c$
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 $T_{\rm e}$ (CAS-SCF MRCI) = 19255 cm⁻¹

 T_{e} (CCSD(T)) = 19478 cm⁻¹

It's what you call "fortuitous"







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



Rovibronic energy level clustering at very high J-values in the $\tilde{X}^2 B_1$ state of SbH₂





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

35



Red A_1 Black A_2 Blue B_1 Green B_2



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