

And now for something completely different...



(Picture courtesy of M. Python)

Simulation of rovibronic spectra for Rennerinteracting electronic states

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Computer programs:

RENNER:

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

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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?

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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:

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

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

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

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



 $\gamma_K(\tau)$

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

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







CH⁺₂ Calculations

- Ab initio potential energy functions from W. P. Kraemer, Per Jensen, and P. R. Bunker, *Can. J. Phys.* 72, 871-878 (1994)
- One parameter of the potential energy function has been adjusted to obtain agreement with experiment for the v_3 vibrational term value in the \widetilde{X}^2A_1 state.

CH⁺₂ **Experiment**

- $\widetilde{X}^2 A_1 v_3$ band ($K_a = 0 \leftarrow 0$ and $1 \leftarrow 1$) measured by M. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, *J. Mol. Spectrosc.* 153, 738-740 (1992).
- Photoelectron spectrum of CH₂; S. Willitsch and F. Merkt: J. Chem. Phys. 118, 2235-2241 (2003).
- $\widetilde{A}^2 B_1 \leftarrow \widetilde{X}^2 A_1$ electronic spectrum; J. L. Gottfried and T. Oka, J. Chem. Phys. 121, 11527 (2004)





























Probability density functions

$$f(r,\tau) = \int_{0}^{\infty} dR \int_{rot,e,es} dV \times |\Psi^{J,M_{J},S,\Gamma_{rve}}|^{2}$$

$$f(\tau) = \int_{0}^{\infty} dr \int_{0}^{\infty} dR \int_{rot,e,es} dV \times |\Psi^{J,M_{J},S,\Gamma_{rve}}|^{2}$$

$$f_{\sigma}(\tau)$$

$$= \int_{0}^{\infty} dr \int_{0}^{\infty} dR \int_{rot,e,es} dV \times |\Psi \sigma| |\Psi^{J,M_{J},S,\Gamma_{rve}}|^{2}$$

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 $\sigma = -$ for the lower (1 ²A^{**} for MgNC/MgCN) state $\sigma = +$ for the upper (2 ²A^{*} for MgNC/MgCN) state





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(a) Probability density functions $f_+(\tau)$ (dashed curve) and $f_-(\tau)$ (dotted curve) from Eq. (38), and (b) the two-dimensional probability density function $f_2(r,\tau)$ [Eq. (41)] for the 104th state with J=1/2 and $\Gamma_{\rm rve}=A''$ of \tilde{A} $^2\Pi \ ^{24}{\rm MgNC}/^{24}{\rm MgCN}$. The corresponding term value is 2834.6 cm⁻¹. For this state, $f_1(\tau) \approx f_+(\tau)$ for $\tau < 90^\circ$ and $f_1(\tau) \approx f_-(\tau)$ for $\tau > 90^\circ$.



Application of DR: HOO/OOH

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ab initio calculations:

 $\widetilde{X}^2 A$ and $\widetilde{A}^2 A$ states

- Program: MOLPRO 2002.6
- Method: Core-valence MR-SDCI+Q/[aug-cc-pCVQZ (O), cc-pVQZ (H)]
- Basis set for hydrogen: Dunning et al.'s correlation consistent valence quadruple zeta basis set (cc-pVQZ),(6s,3p,2d,1f)/ [4s,3p,2d,1f]
- Basis set for oxygen: Dunning et al.'s augmented correlation consistent polarized core-valence valence quadruple zeta basis set (aug-cc-pCVQZ),(16s,10p,6d,4f,2g)/[9s,8p,6d,4f,2g]











Simulation of HOO $\widetilde{A}^2 A' \leftarrow \widetilde{X}^2 A''$ absorption spectrum





Application of RENNER: SbH₂

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ab initio calculations:

- 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





Simulation of ¹²¹SbH₂ \widetilde{X}^2B_1 absorption spectrum

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T = 300 K $N \le 10$ $J \le 19/2$





Table 8: 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	$\nu_1/{\rm cm}^{-1}$	ν_3/cm^{-1}	
SbH_2	pure H_2	1869.7	1878	
	${\rm Ne}/{\rm H_2}$	1879.0	1883.9	
	$\mathrm{Ar/H_2}$	1863.7	1869.0	Δ
$^{121}\mathrm{SbH}_2$	$\operatorname{Calc.}^{a}$	1889.1	1892.1 <	Present work
SbD_2	pure D_2	1341.9	1345.8	7
	${ m Ne}/{ m D}_2$	1349.4	1352.0	
	$\rm Ar/D_2$	1337.6	1341.8	4
$^{121}\mathrm{SbD}_2$	$\operatorname{Calc.}^{b}$	1357.8	1360.6	Present work
$\rm SbHD$	Ar/HD	1339.6	1866.5	1
$^{121}\mathrm{SbHD}$	$\operatorname{Calc.}^{c}$	1359.0	1890.7 <	Present work

[19] X. Wang, P. F. Souter and L. Andrews, J. Phys. Chem. A. 107 (2003) 4244-4249; matrix isolation infrared spectroscopy.



Simulation of ¹²¹SbH₂ $\widetilde{A}^2A_1 \leftarrow \widetilde{X}^2B_1$ absorption spectrum

T = 300 K $N \le 10$ $J \le 19/2$





Table 7: 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 the calculated positions $\tilde{\nu}_{calc}$ (cm⁻¹) of the strongest line in each Q branch of ¹²¹SbH₂ with $v_2'' = 0.^a$

v'_2	$\tilde{\nu}_{\mathrm{obs}}$	$\tilde{\nu}_{\mathrm{calc}}$	$O-C^b$	$\delta_{\rm obs}{}^c$	δ_{calc}^{d}	$\tilde{A}(0, v_2', 0)^e$
0	19438	18316	1122	0	0	0
1	20131	18932	1199	693	616	616.0
2	20822	19592	1230	1384	1276	1276.0
3	21511	20267	1244	2073	1951	1950.6
4	22191	20920	1271	2753	2604	2604.2
5	22863	21561	1302	3425	3245	3244.8
6	23529	22218	1311	4091	3902	3901.6

 ${}^{a}v'_{2}$ pertains to the $\tilde{A}^{2}A_{1}$ state and v''_{2} to the $\tilde{X}^{2}B_{1}$ state. ${}^{b}\tilde{\nu}_{obs} - \tilde{\nu}_{calc}$, in cm⁻¹. ${}^{c}\delta_{obs} = \tilde{\nu}_{obs} - 19438 \text{ cm}^{-1}$, in cm⁻¹. ${}^{d}\delta_{calc} = \tilde{\nu}_{calc} - 18316 \text{ cm}^{-1}$, in cm⁻¹. e Calculated term value (in cm⁻¹) of the $\tilde{A}(0, v'_{2}, 0)$, $(N_{K_{a}K_{c}}, J) = (0_{00}, 1/2)$ level of 121 SbH₂ [relative to the $\tilde{A}(0, 0, 0)$, $(N_{K_{a}K_{c}}, J) = (0_{00}, 1/2)$ level].

[20] N. Basco and K. K. Lee, Spectroscopy Letters 1 (1968) 13-15; flash photolysis of stibine (SbH₃).



Energy clusters: ¹²¹SbH₂ \widetilde{X}^2B_1 vibrational ground state











${}^{121}SbH_2 \text{ and } {}^{123}SbH_2 \\ \widetilde{A}{}^2A_1 \rightarrow \widetilde{X}{}^2B_1 \text{ emission}$ spectrum

Experiment: T. Ni, S. Yu, X. Ma and F. Kong, Chem. Phys. Lett. 128 (1986) 270-273. Intensity in arbitrary units

ArF laser photolysis of SbH₃.

Red: Resolution 3 Å

Blue: Resolution 12 Å

Simulation:

T = 1200 K

 $N \leq 25$ $J \le 49/2$





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