

(Picture courtesy of
M. Python)

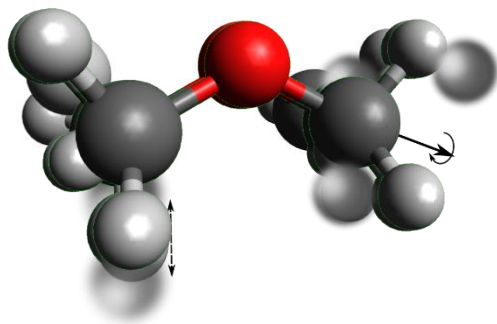
Making headway in understanding the rotation- vibration spectrum of protonated methane CH_5^+ - an extremely flexible molecule

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Rovibrational motion in cold molecules: Example: dimethyl ether



Motion in cold molecules

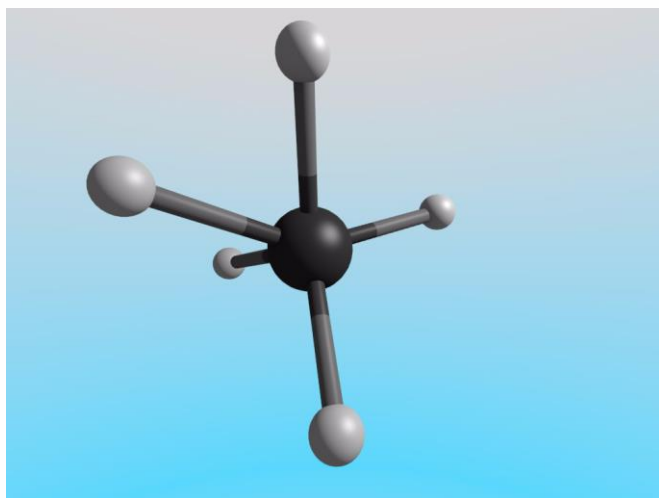
- Born-Oppenheimer approximation
(Electronic ground state)
- Overall rotations
- Small amplitude vibrations
- Large amplitude vibrations
(e.g., internal rotations)

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

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

Beyond rotation-vibration separation: Extremely flexible protonated methane

“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]

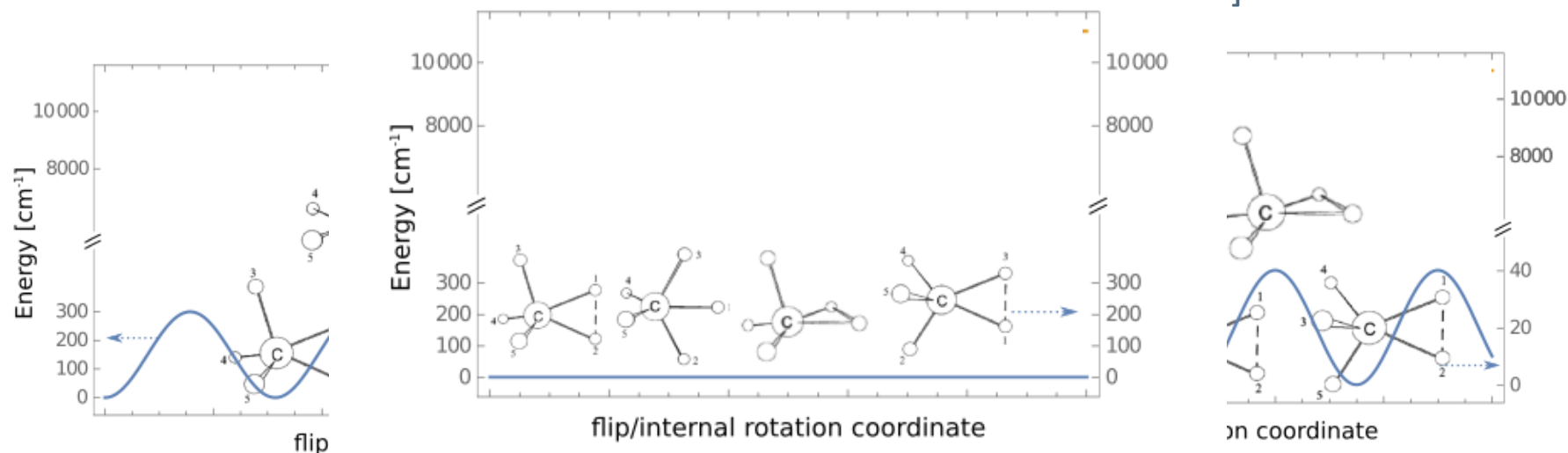
~~$$\hat{H}_{\text{full}} = \hat{H}_{\text{rot}} + \hat{H}_{\text{LAV}} + \hat{H}_{\text{SAV}}$$
$$|\psi_{\text{full}}\rangle = |\psi_{\text{rot}}\rangle |\psi_{\text{LAV}}\rangle |\psi_{\text{SAV}}\rangle$$~~

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



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

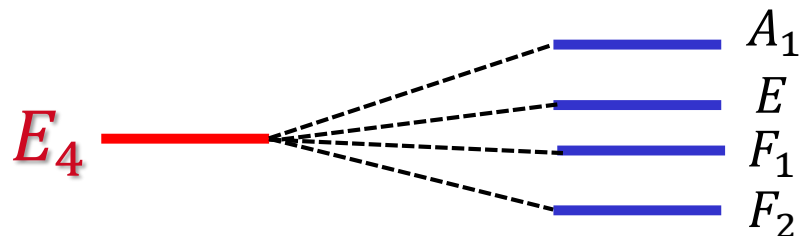
Our starting point: Completely flat potential

Pedagogical example for better understanding: Rigid methane

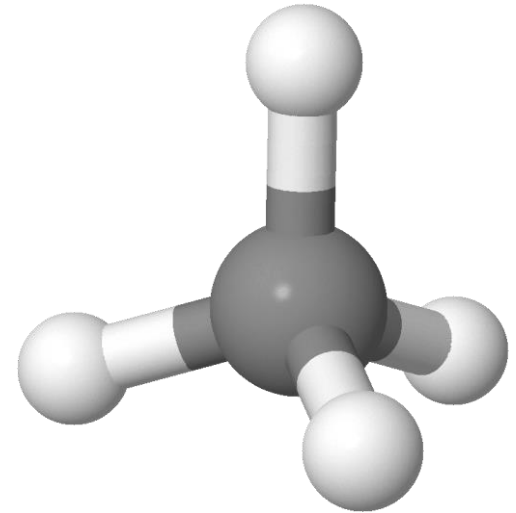
- **Non-vibrating, static methane molecule = rigid spherical top**
- Hamiltonian: $\hat{H} = B(\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2)$
- Full rotational symmetry: Group $\mathbf{K}(\text{mol})$, isomorphic to $\text{SO}(3)$
- Irreducible representations $D_J, J = 0, 1, 2, 3, 4, \dots$

$$E_J = B J(J + 1)$$

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



Labeled by
irreducible
representations of
 $T_d(\text{M}) \subset \text{SO}(3)$



Permutation/inversion symmetry in protonated methane

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

- 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

The character table of the group S_5

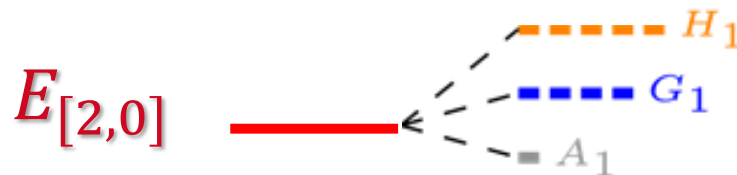
	E	(12)	$(12)(34)$	(123)	$(12)(345)$	(1234)	(12345)
	1	10	15	20	20	30	24
$A_1 :$	1	1	1	1	1	1	1
$A_2 :$	1	-1	1	1	-1	-1	1
$G_1 :$	4	2	0	1	-1	0	-1
$G_2 :$	4	-2	0	1	1	0	-1
$H_1 :$	5	1	1	-1	1	-1	0
$H_2 :$	5	-1	1	-1	-1	1	0
$I :$	6	0	-2	0	0	0	1

Pedagogical example continued: Protonated methane simplified

- 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 $[n_1, n_2]$, $n_1 \geq n_2 = 0, 1, 2, 3, 4, \dots$

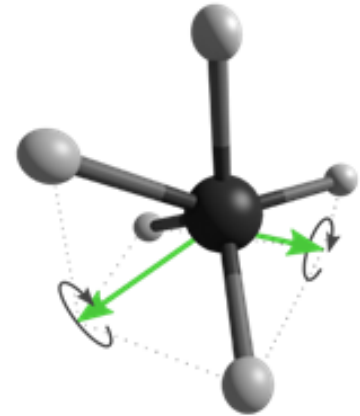
$$E_{[n_1, n_2]} = \frac{B}{2} \{n_1(n_1 + 3) + n_2(n_2 + 1)\}$$

- 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)



Electric dipole moment selection rules in $SO(5)$

- Space-fixed components of dipole moment has symmetry A_1 in S_5
- Assumption: In $SO(5)$ there are contributions from all $[n_1, n_2]$ that image onto A_1 by forward correlation

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

$$([n'_1, n'_2] \otimes [n_1, n_2]) \downarrow S_5 \supset A_1$$

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

Molecular super-rotor: Algebraic theory re-invented

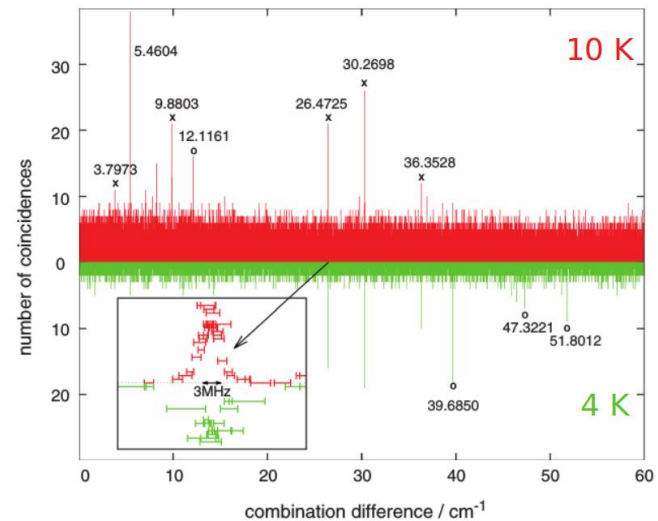
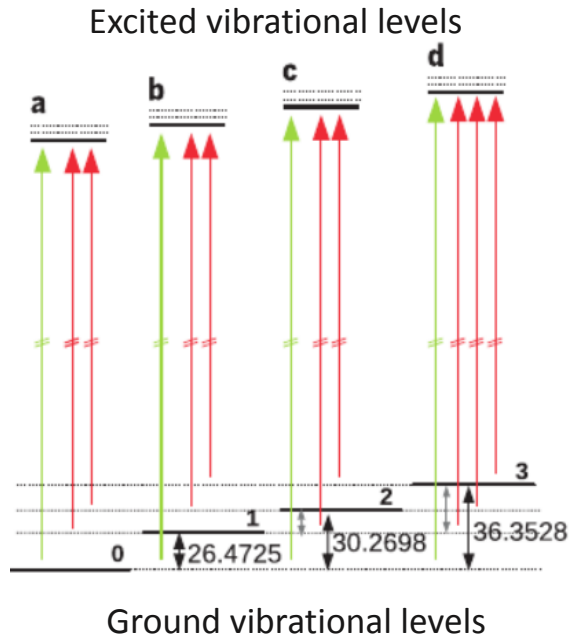
Developed theory has great similarity to the algebraic theory by Iachello and co-workers^{*,**}

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).

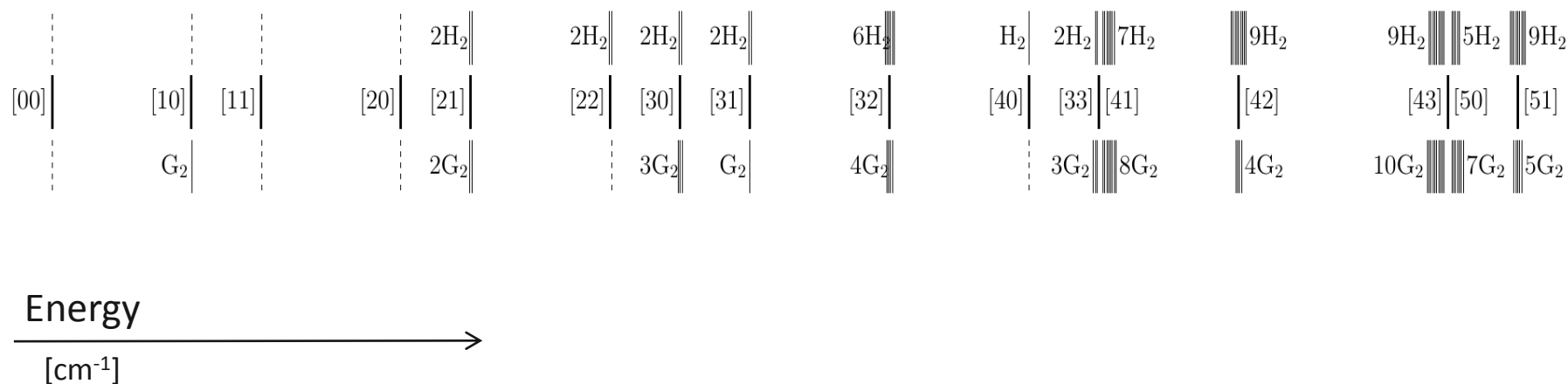
**F. Iachello, R.D. Levine, Algebraic theory of molecules, in: Topics in Physical Chemistry, Oxford University Press, 1995.

Rovibrational energies of CH_5^+ from experiment: Combination differences



- 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]

Direct comparison of theory and experiment



Dashed arrows are experimental GS combination differences

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

Comparison to experiment II

Symmetry S_5	Exp. CoDiffs [cm ⁻¹]	Present work [cm ⁻¹]	Assignment 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])
H_2	55.17916**	55.10	[2,1] - [5,1]
	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)

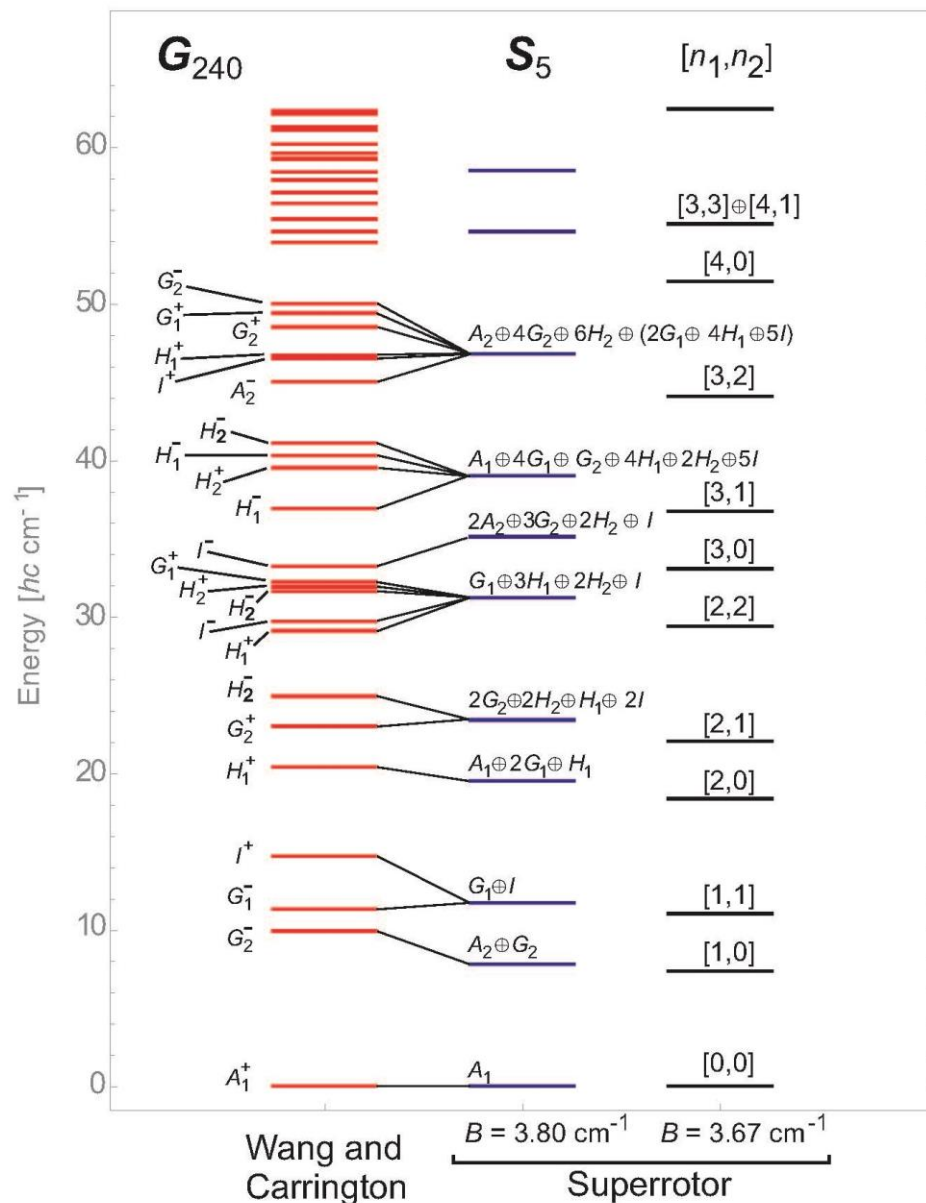
(*) And (**) have been identified in the CoDiff spectrum only recently

(Brackertz, S; Diploma thesis; University of Cologne; 2016)

Comparison with conventional QM calculations

X.-G. Wang, T. Carrington, Vibrational energy levels of CH_5^+ , *J. Chem. Phys.* **129** 234102, (2008)

X.-G. Wang, T. Carrington, Calculated rotation-bending energy levels of CH_5^+ 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
- Comparison to other models

Protonated methane

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

Dramatis personæ



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](https://doi.org/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](https://doi.org/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](https://doi.org/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](https://doi.org/10.1016/j.jms.2017.06.002)



Many thanks for your attention!