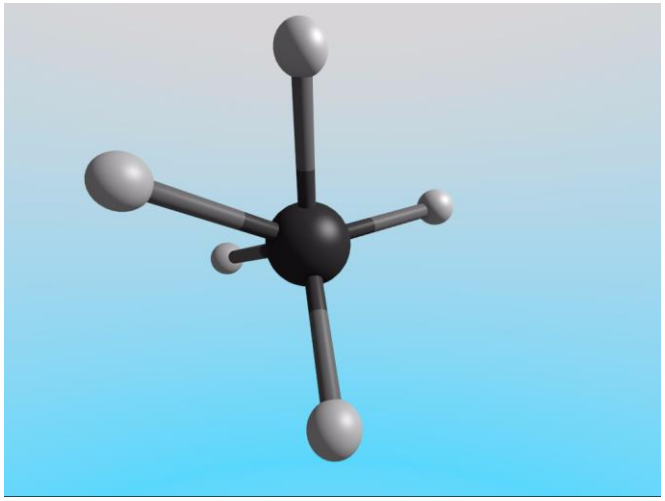
Beyond rotation-vibration separation: Extremely flexible protonated methane

"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 CH_5^+

- Five protons but four bonds
- No well-defined, static equilibrium geometry
- Internal rotations & flips

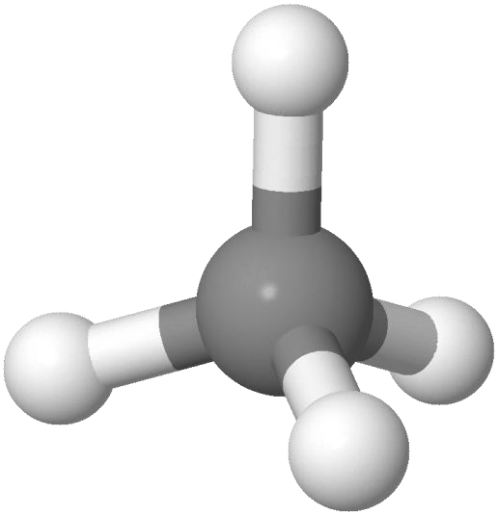
⇨ Rotation and vibration inseparable [2]

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

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)

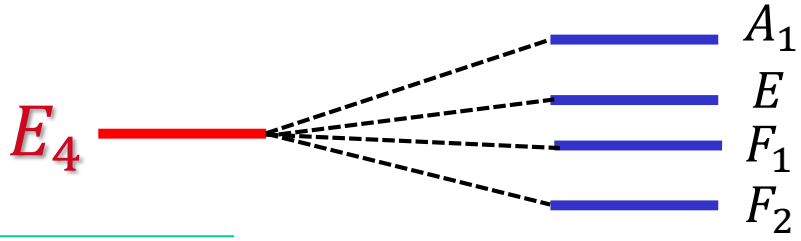
Pedagogical example for better understanding: Rigid methane



- **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 $\boldsymbol{K}$(mol), isomorphic to SO(3)
- Irreducible representations $D_J, J = 0, 1, 2, 3, 4, \ldots.$

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

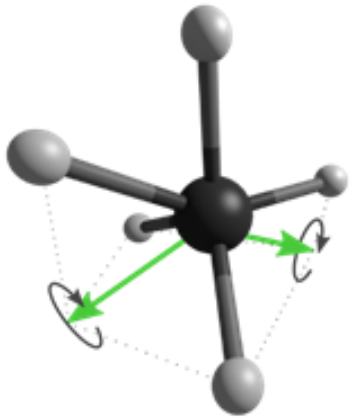
- **Vibrating, actually existing methane molecule**
- Molecular symmetry group $\boldsymbol{T}_\mathrm{d}(\mathrm{M}) \subset \mathrm{SO}(3)$



Labeled by irreducible representations of $\boldsymbol{T}_\mathrm{d}(\mathrm{M}) \subset \mathrm{SO}(3)$

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

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 $[n_1, n_2], \quad n_1 \geq n_2 = 0, 1, 2, 3, 4, \ldots.$

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

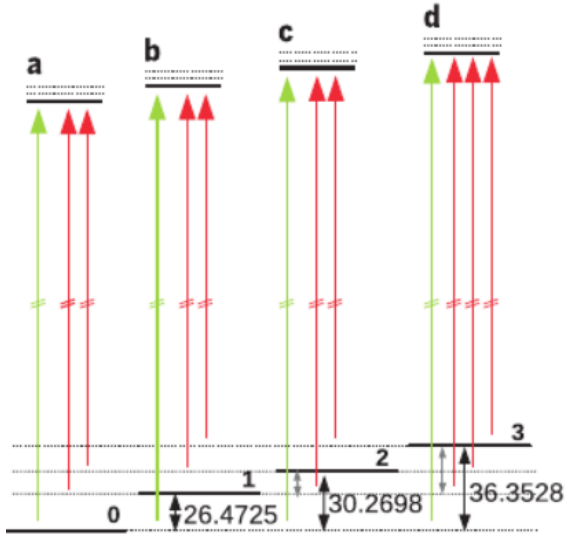
- **Fully vibrating, actually existing protonated methane molecule**
- Molecular symmetry group $\boldsymbol{G}_{240} \subset \mathrm{SO}(5)$

Labeled by irreducible representations of $\boldsymbol{G}_{240} \subset \mathrm{SO}(5)$

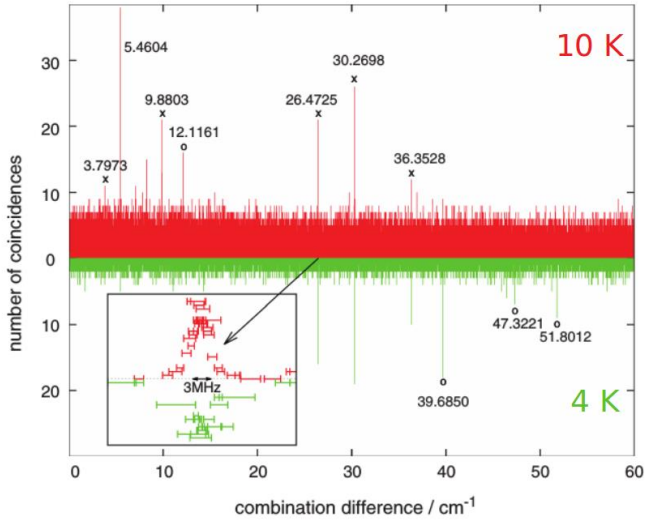
[4] e.g.. Racah, G.; *Phys Rev.* **76**, 1352, (1949)

Rovibrational energies of CH_5^+ from experiment: Combination differences

Excited vibrational levels



Ground vibrational levels

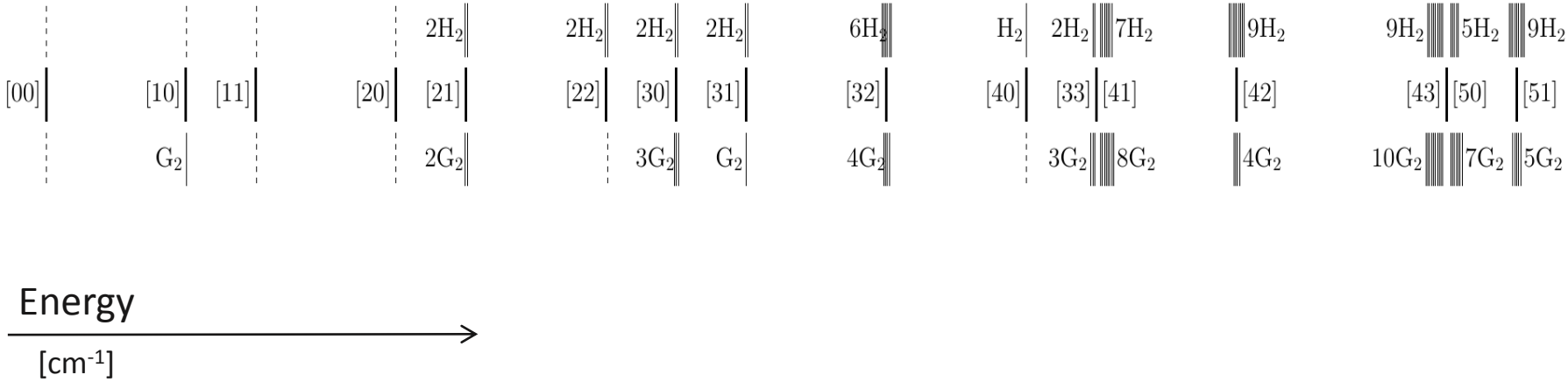


- Scan rovibrational transitions (infrared)
- Construct the differences of all transitions (Combination differences = CoDiffs)
- If two transitions share upper level, this CoDiff occurs regularly (many upper states!)

➡ Differences rebuild ground state energy levels [6]

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

Direct comparison of theory and experiment



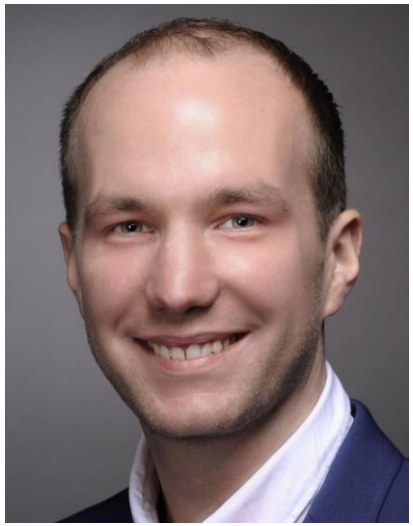
Energy

[cm^{-1}]

Dashed arrows are experimental GS combination differences

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

Dramatis personæ



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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*

Many thanks for your attention!