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
  \[ \text{ Rotation and vibration inseparable } [2] \]

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

First observation: Free internal rotation angle and axis!

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 $K(\text{mol})$, isomorphic to $\text{SO}(3)$
- 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 $T_d(M) \subset \text{SO}(3)$

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 \([n_1, n_2]\), \( n_1 \geq n_2 = 0, 1, 2, 3, 4, \ldots \)

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

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

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

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

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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

**Ponderers** (answer phone, pontificate…)

Hanno Schmiedt  
Principal doer

Stephan Schlemmer

Per Jensen

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Many thanks for your attention!