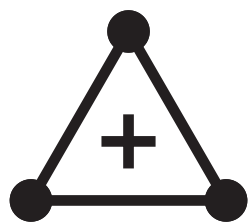


Compilation and Evaluation of the Laboratory Spectroscopy of H_3^+

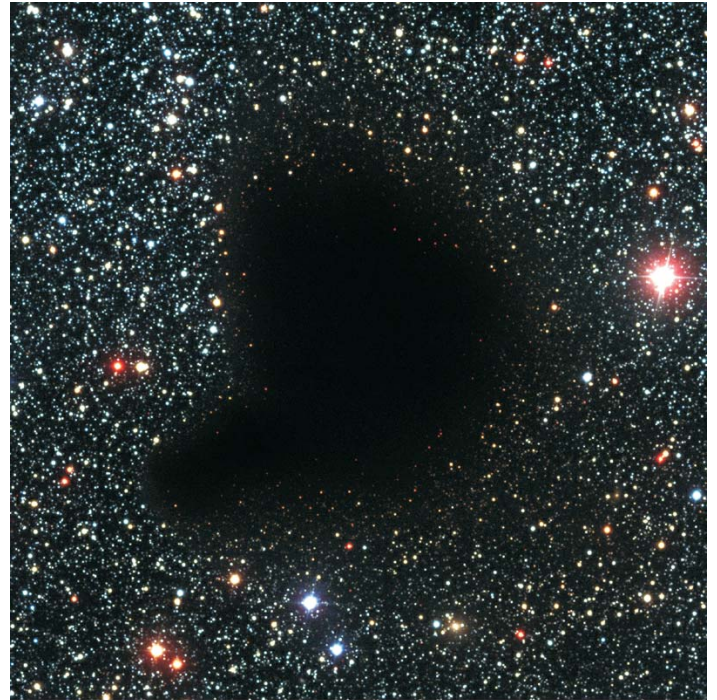


Mike Lindsay and Ben McCall

**Oka Ion FactoryTM
University of Chicago**

Why is H_3^+ Important?

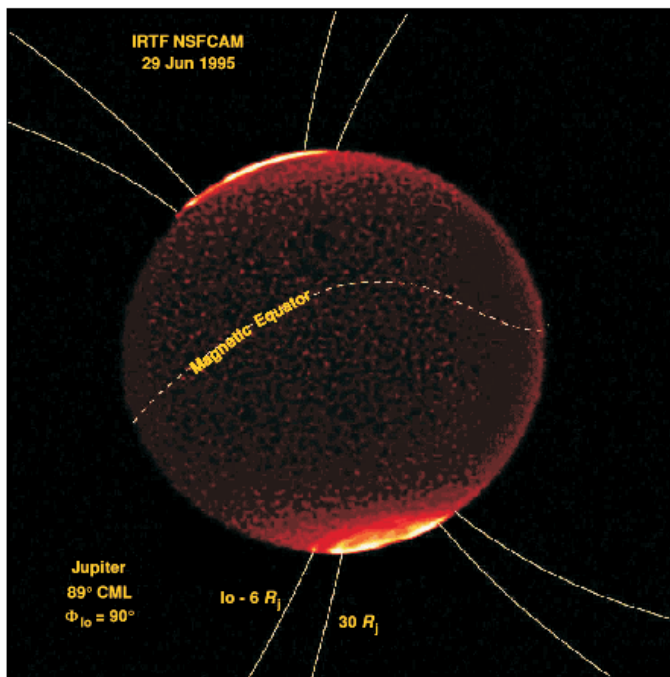
- Initiates the chemistry in interstellar clouds



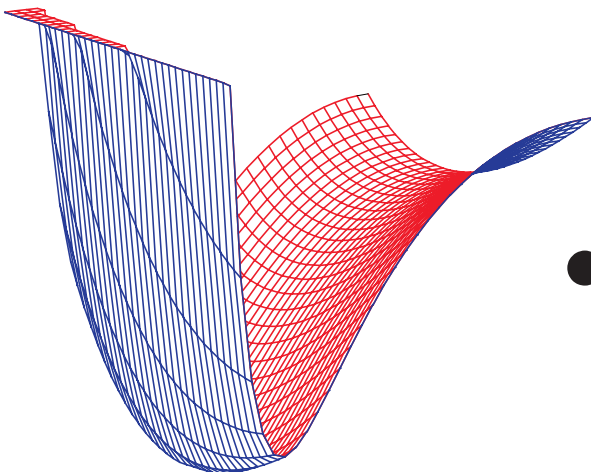
ESO PR Photo 20a.99 (30 April 1999)

The "Black Cloud" B68
(VLT ANTU + FORS1)

© European Southern Observatory



- Useful probe of the conditions in laboratory and space plasmas



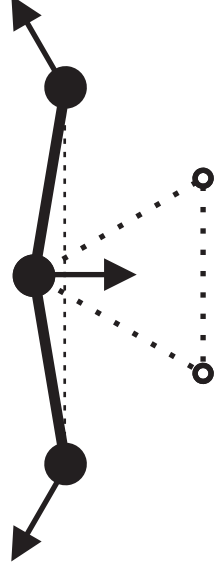
- As the simplest polyatomic molecule, it is a benchmark for *ab initio* theory

H₃⁺ : An Interesting Quantum System

- Simplest polyatomic molecule: 3 protons, 2 electrons

- Non-classical bonding

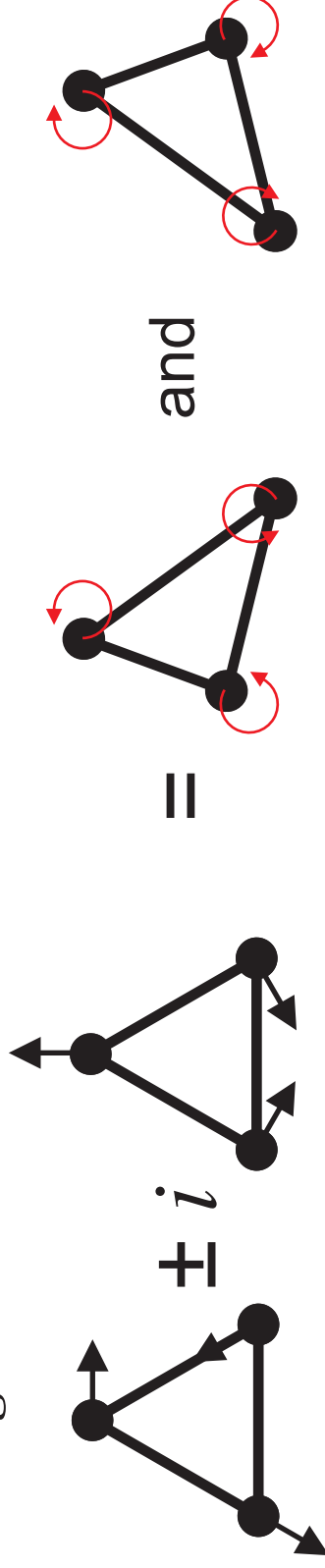
- Kinetic energy singularity at the barrier to linearity



- Low mass Born-Oppenheimer approx. breakdown

- Anharmonic potential

- Strong Coriolis interaction

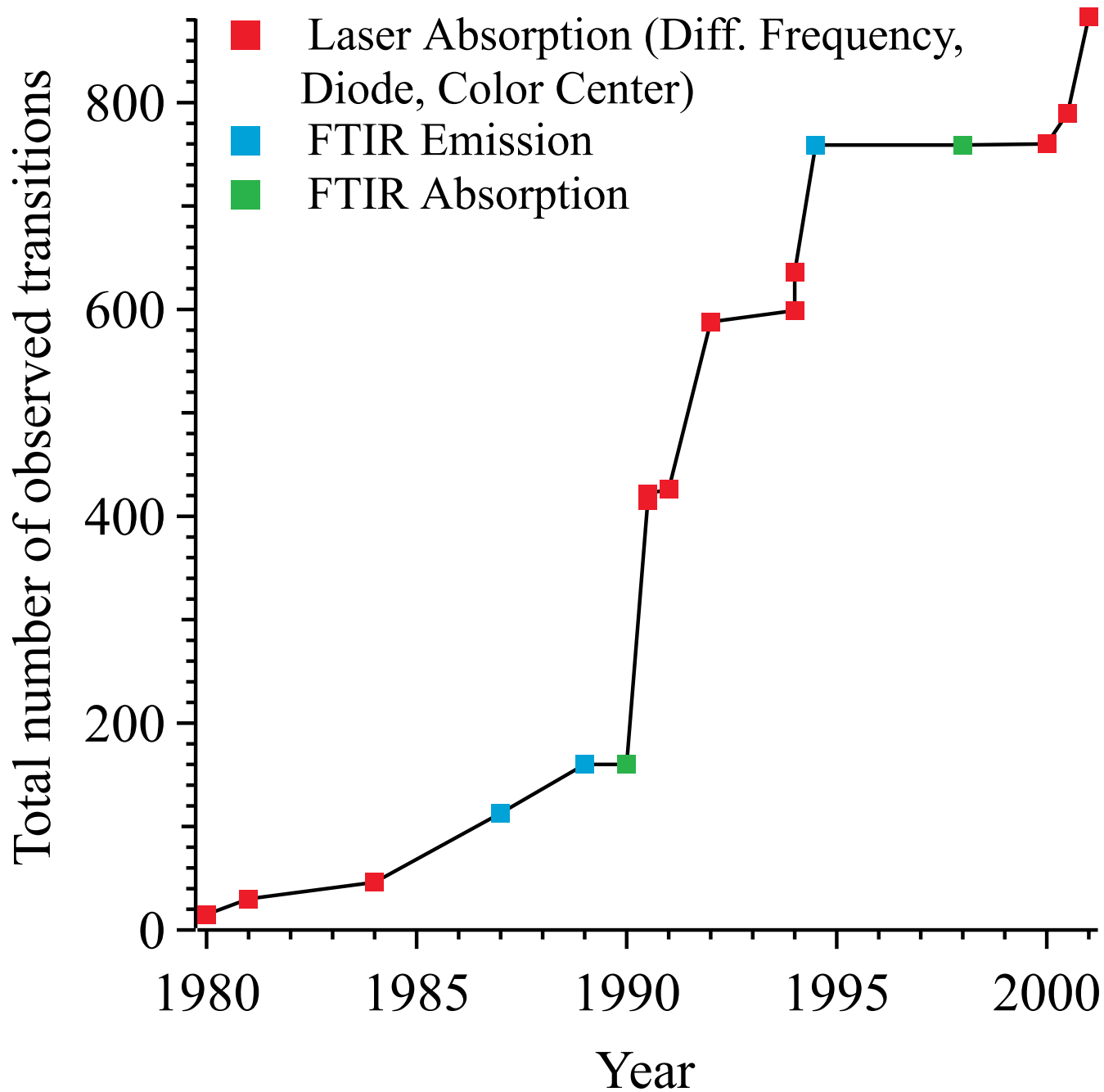


- Quantum Numbers:

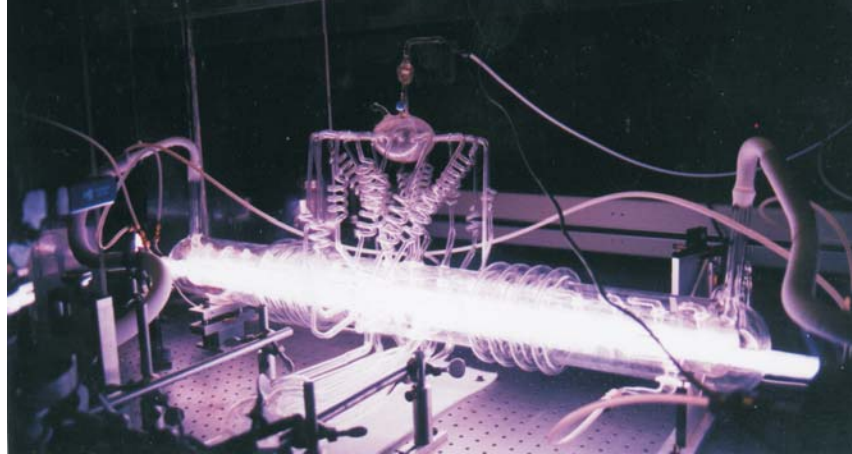
“Good QN’s”: J, I , and \pm

“Approximate QN’s”: $\nu_1, \nu_2, \ell, G = |k - \ell|$

Two Decades of Spectroscopy



Current State of Affairs:



LAB

- 895 transitions / 17 experiments
- Multiple measurements
- Conflicting assignments
- Uncertainty underestimation

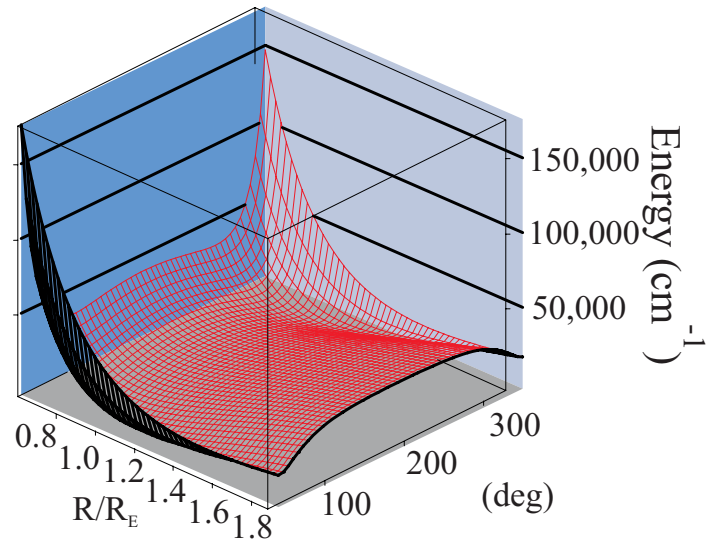


SPACE



Telescope Spectrometer
Resolution $\sim 0.03 \text{ cm}^{-1}$

THEORY



H_3^+ potential energy surface
accuracy $\sim 0.02 \text{ cm}^{-1}$

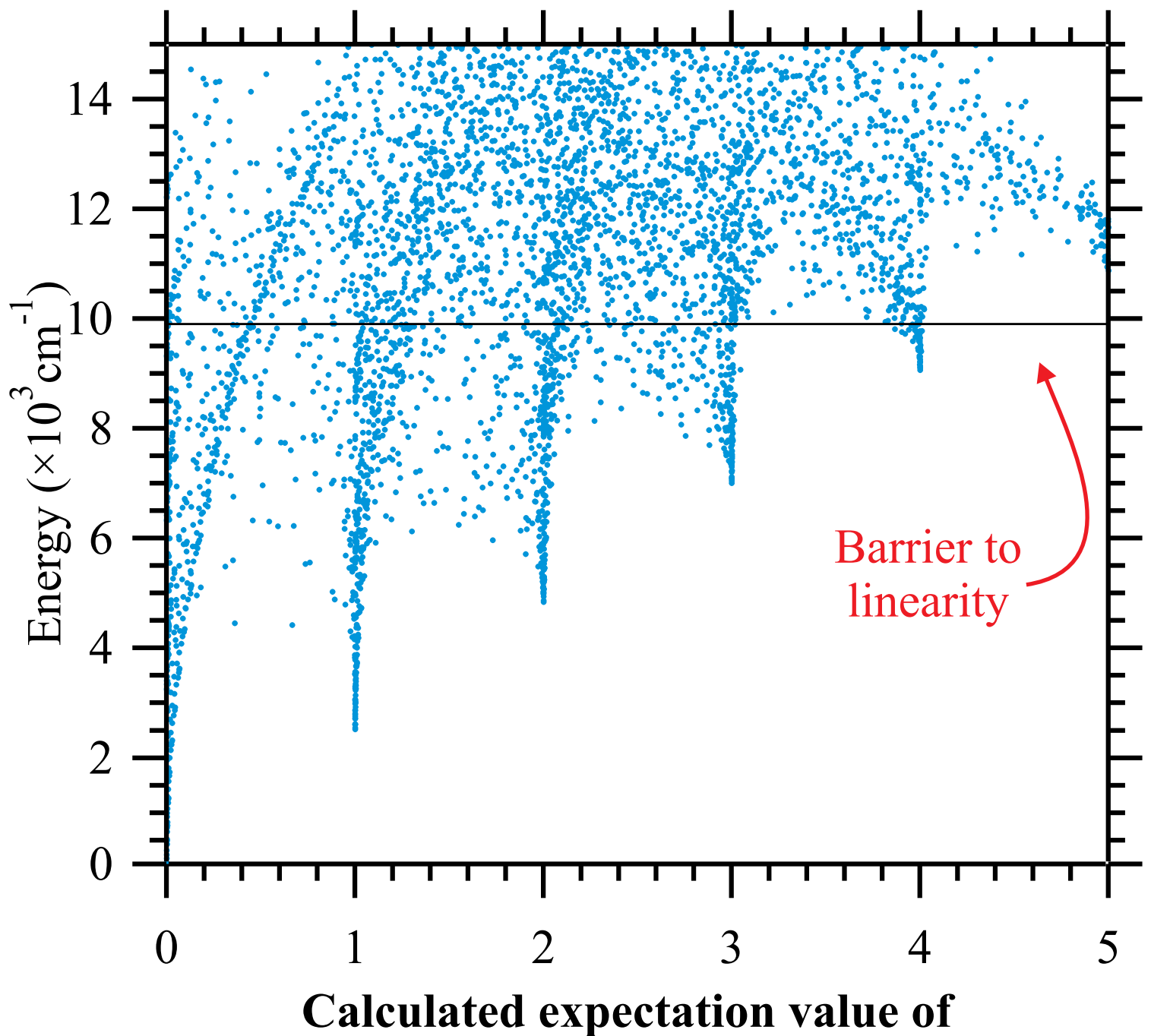
Goals of Our Work



- **“Unambiguously” label all levels $< 9000 \text{ cm}^{-1}$**
- **Reassign all lines (frequency and intensity)**
- **Confirm assignments (combination differences)**
- **Derive experimentally determined energy levels**
- **Compare energy levels with theory**

Labels for levels below 9000 cm^{-1}

- Strong mixing hinders easy labeling G, ℓ, ν_1, ν_2
- Treat the approximate quantum numbers as an observable and calculate its expectation value

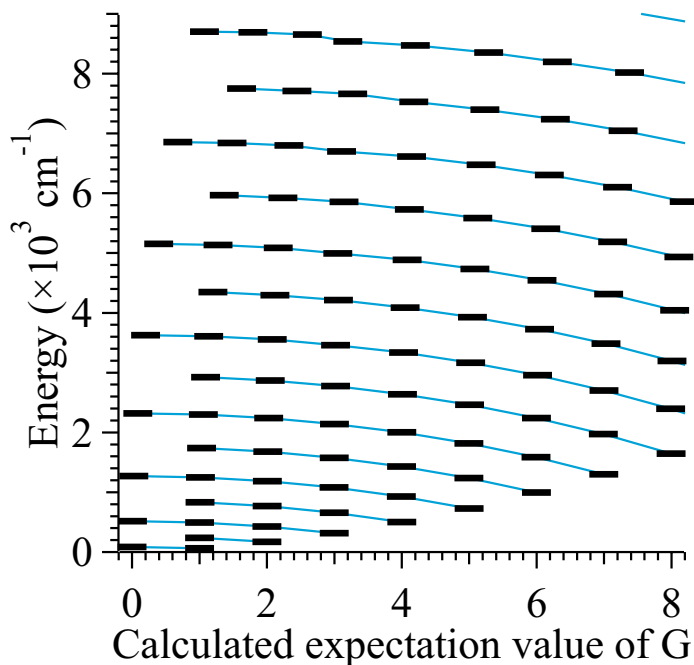


From calculations of Jim Watson

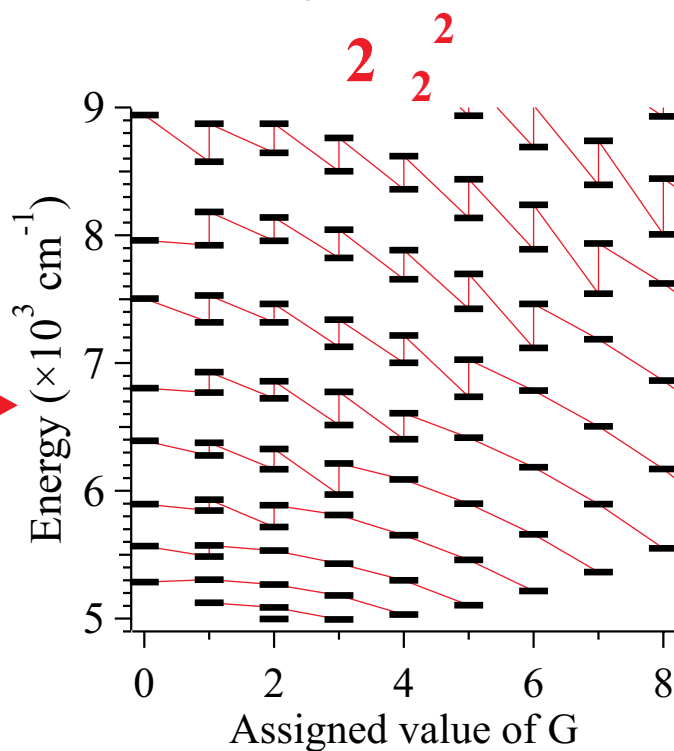
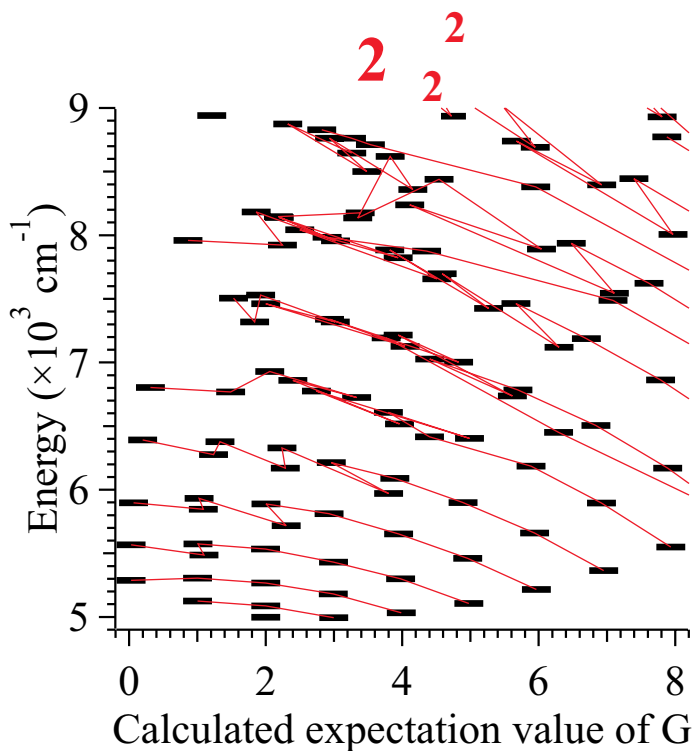
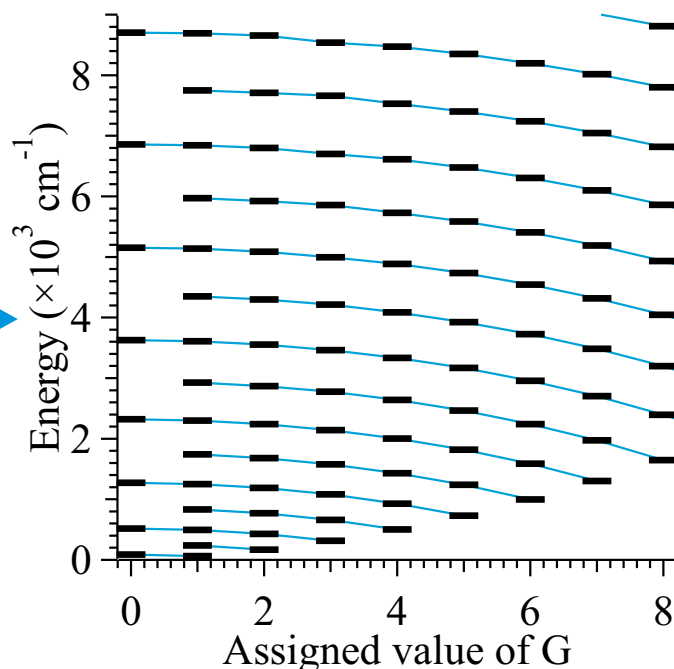
Labels for levels below 9000 cm^{-1}

- We simultaneously considered all levels
- Identify dominant contribution to the mixing
- Few states too badly mixed for meaningful labels

Ground State

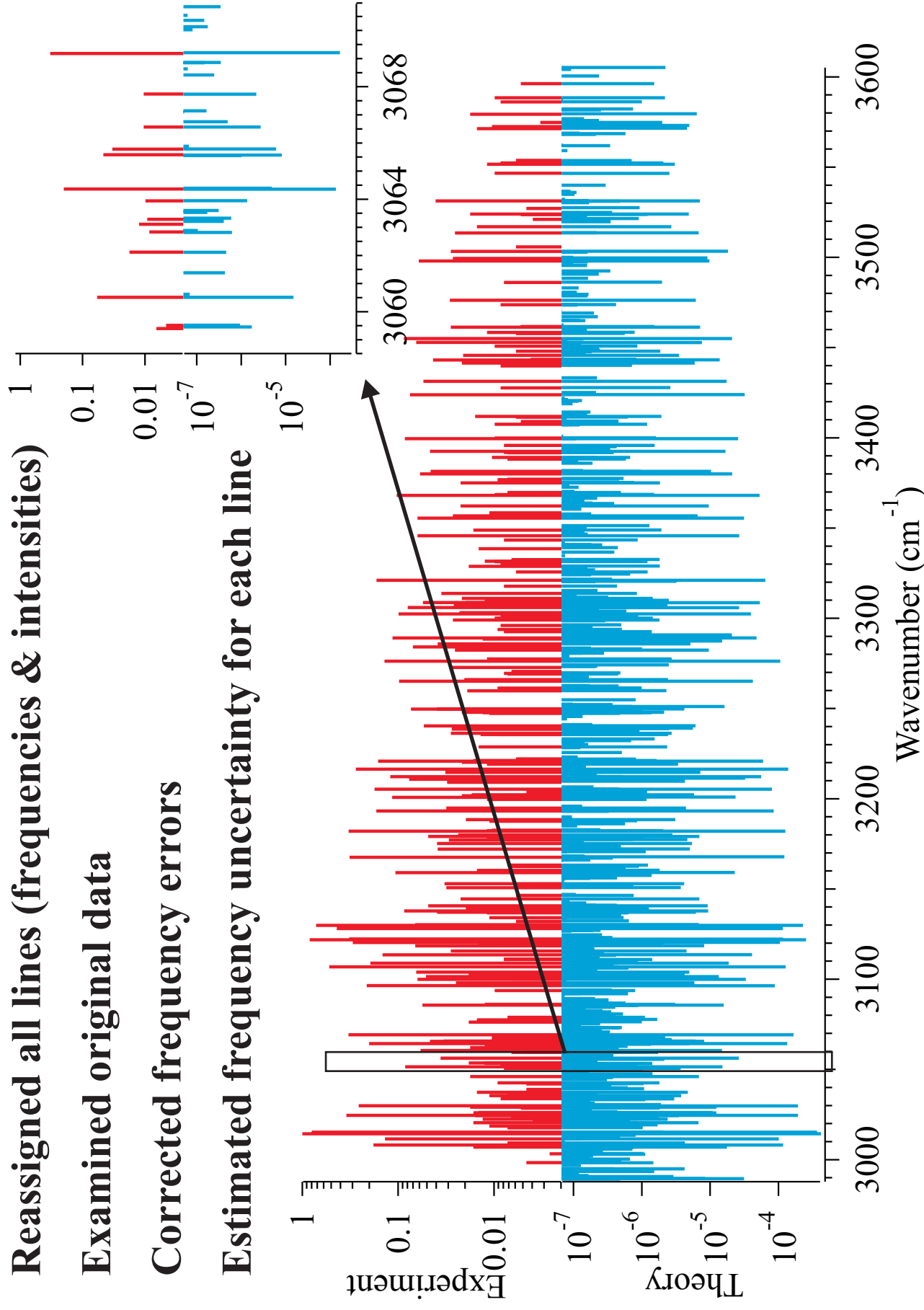


Ground State

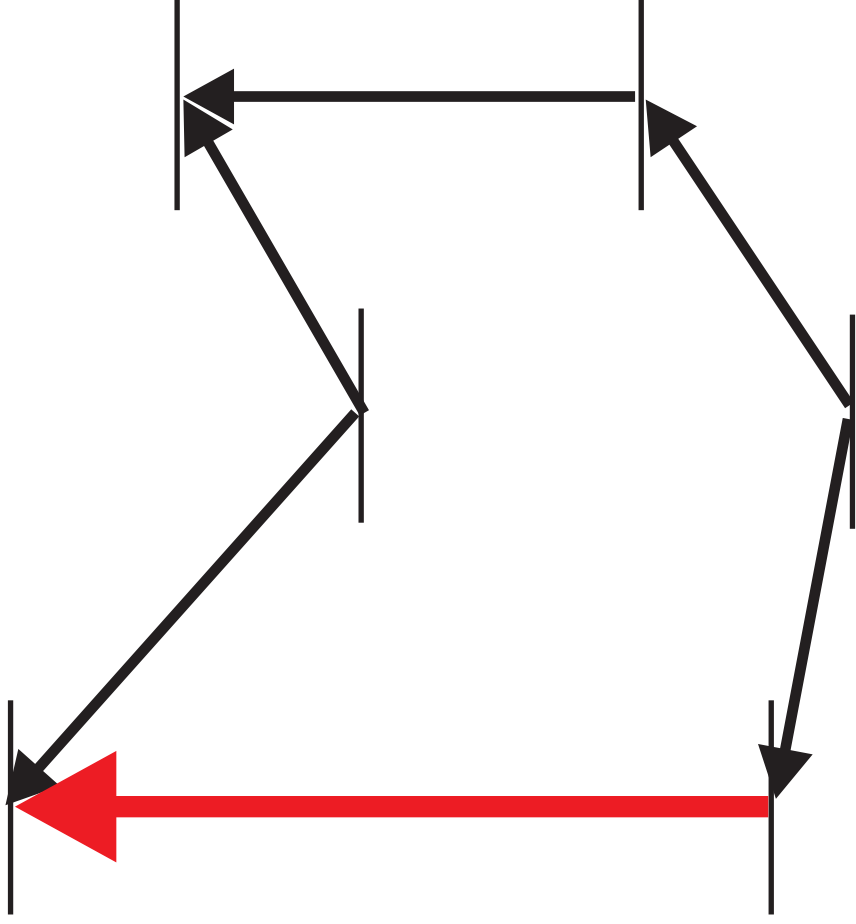


Reassignment of Transitions

- Reassigned all lines (frequencies & intensities)
- Examined original data
- Corrected frequency errors
- Estimated frequency uncertainty for each line

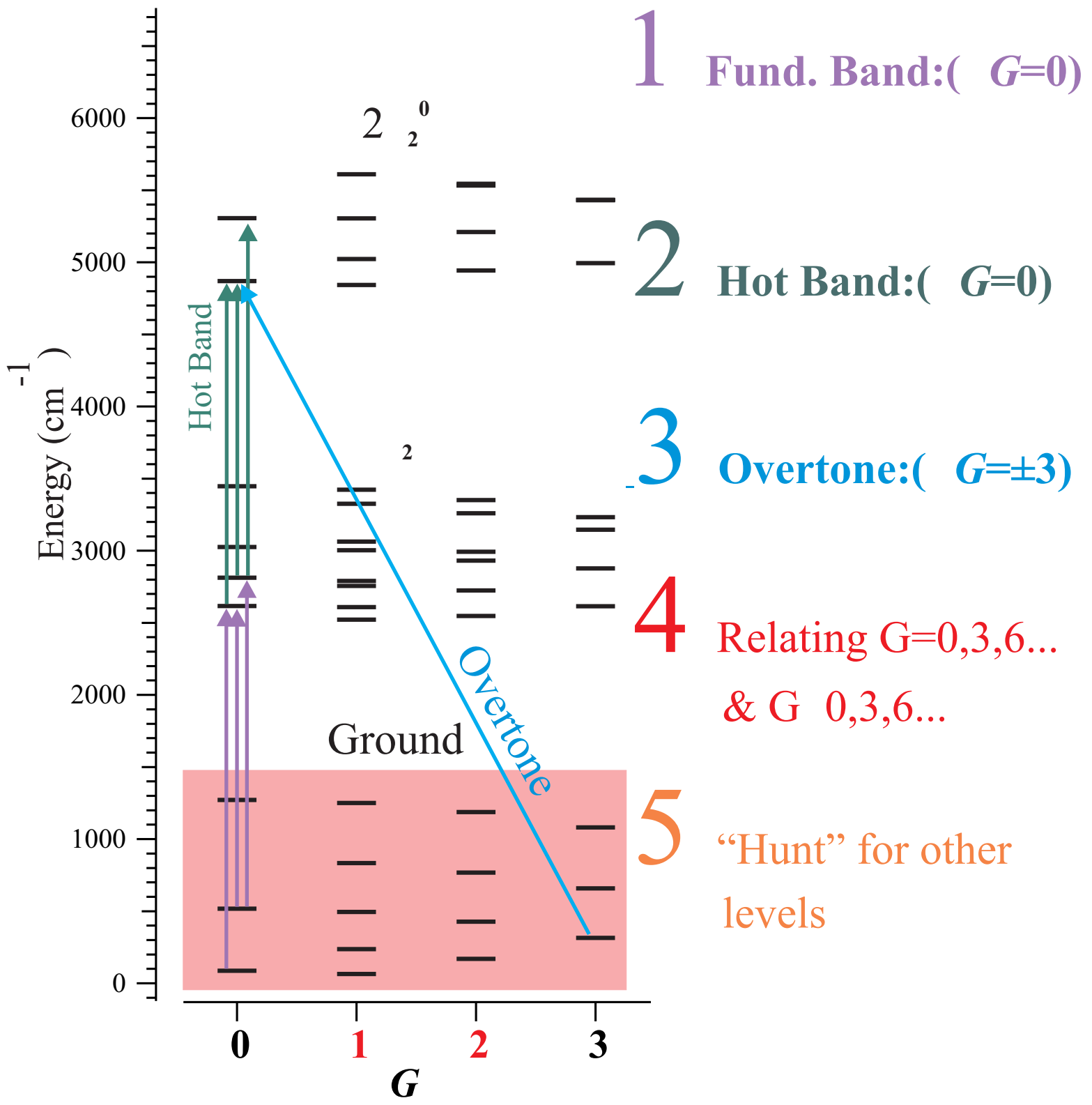


Combination Differences



- Program automatically searches for combination differences
- Considered paths up to 7 transitions long
- All agree to $<1.5 \times$ uncertainty

Exp. Determined Energies Levels



1 Fund. Band: ($G=0$)

2 Hot Band: ($G=0$)

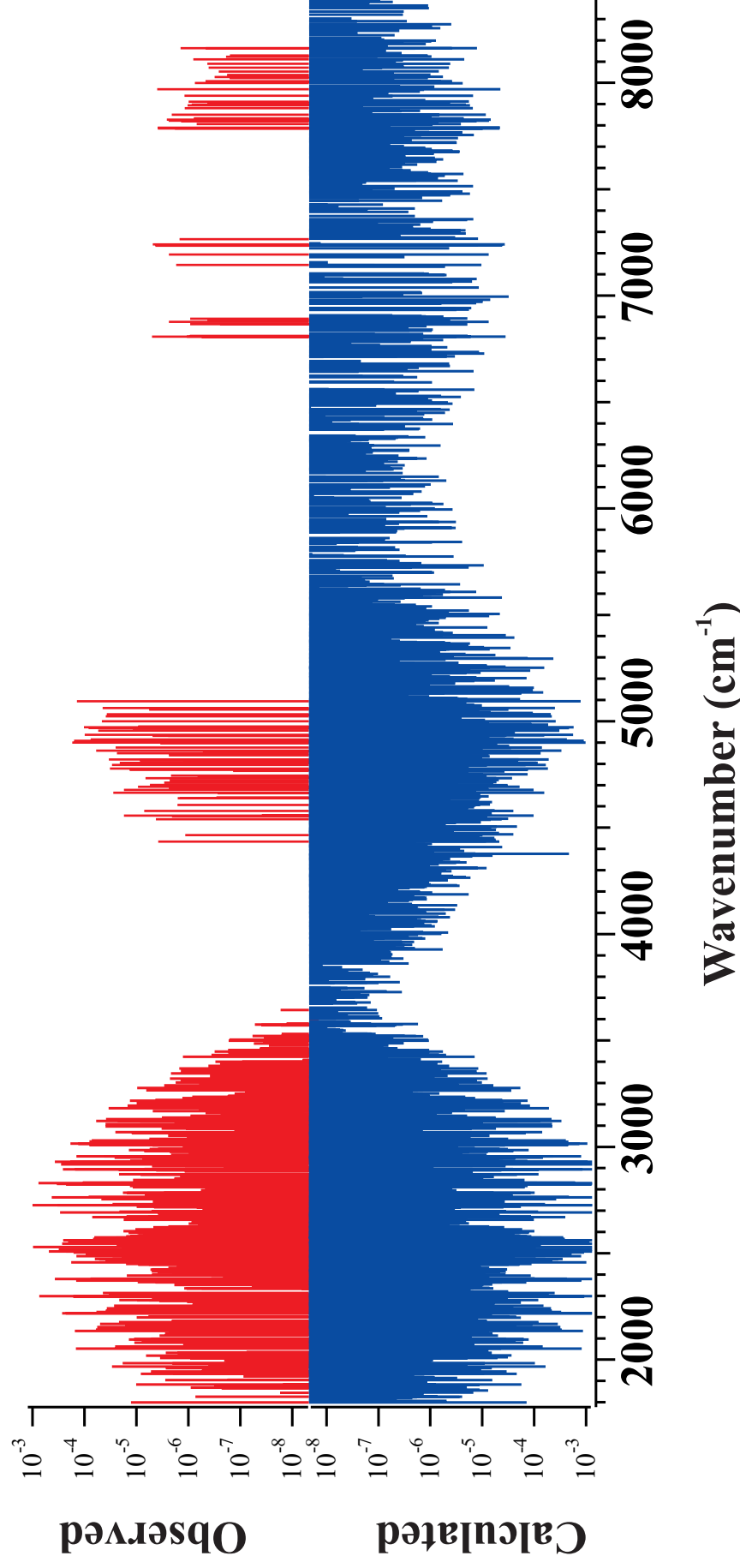
3 Overtone: ($G=\pm 3$)

4 Relating $G=0,3,6\dots$
& $G 0,3,6\dots$

5 "Hunt" for other
levels

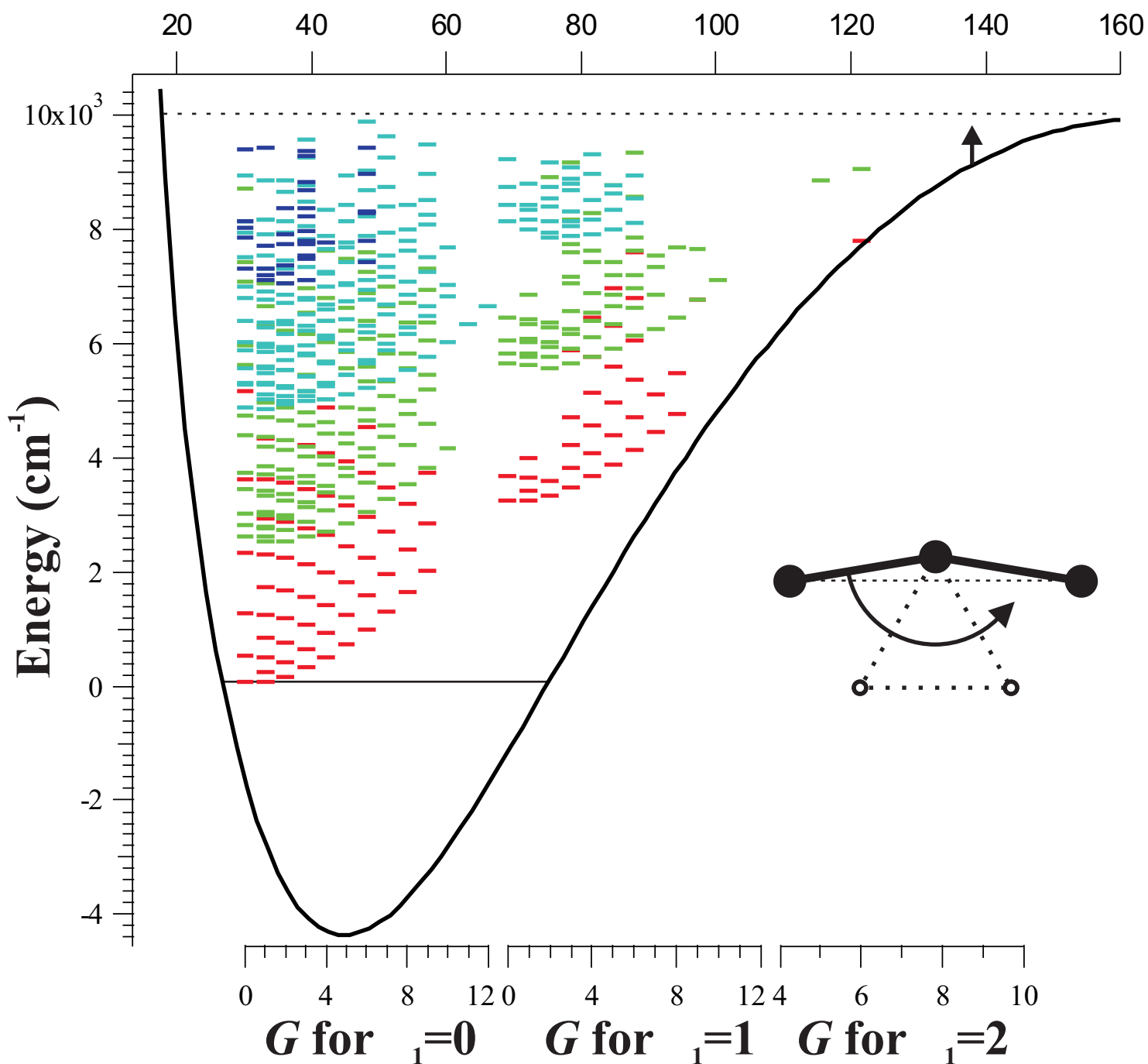
Summary of Transitions

- 823 confident assignments (from 895 reported)
- 486 confirmed by combination differences

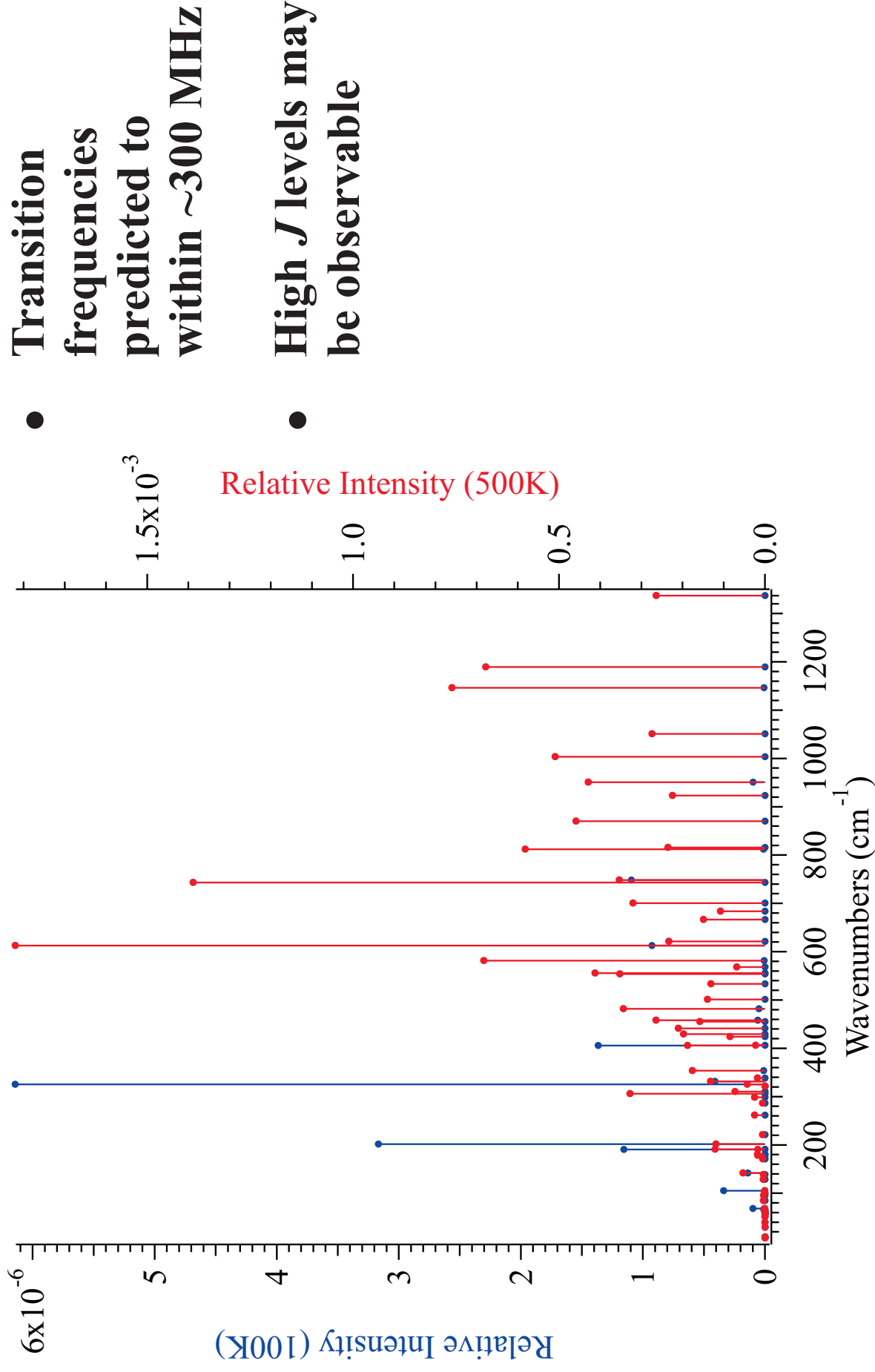


Summary of Energy Levels

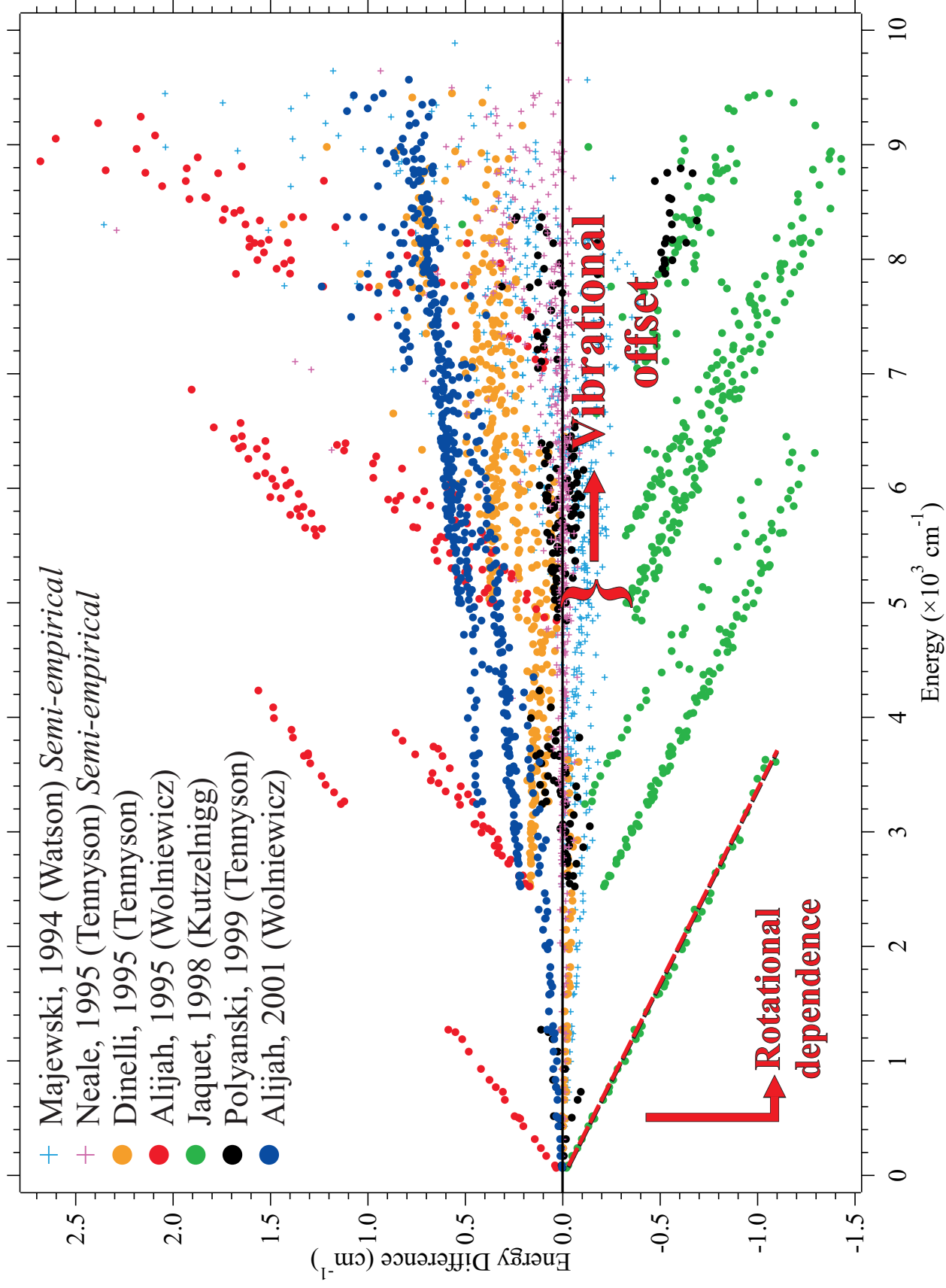
- 526 energy levels determined
- 270 determined only with comb. diff. transitions
- Completely independent of theory



The Forbidden Pure Rotation Spectrum of H_3^+



Analysis of *ab initio* Theory



Summary

- Energy level labeling scheme up to 9000 cm^{-1}
- 823 assigned transitions
- 526 determined energy levels
- Pure rotational spectrum predicted
- Powerful tool to characterize ro-vibrational calculations
- All data available online at:
<http://h3plus.uchicago.edu/>

Acknowledgements...

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