

FROM LINES TO STATES WITHOUT A MODEL

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The fundamental Ritz combination principle ^a originally found for atoms has also been applied to molecules as a method to reconstruct the energy states from measured lines without relying on any model Hamiltonian. In 2006 Nesbitt and coworkers ^b proposed to apply it to protonated methane, CH₅⁺. We used this idea to reconstruct a part of its ground state energies employing spectra of combination differences (CDs) determined from very high resolution ro-vibrational data ^c. Since then the method has been significantly improved ^d as the CD lines essentially represent kernel density estimations, a well-known tool in mathematics. Furthermore, a combinatorial approach has been developed to reconstruct vibrational ground states as well as vibrationally excited states from the CD spectra without relying on measurements at different temperatures. As a result, 1063 of the 2897 measured lines of CH₅⁺ being part of four different symmetry species could be assigned. This allowed for a comparison of the measurements with the analytical model of Schmiedt et al. ^e as well as with the *ab initio* calculations of Wang and Carrington ^f.

^aW. Ritz, On a new law of series spectra, *Astrophys. J.* 28 (1908) 237.

^bC. Savage, F. Dong, D.J. Nesbitt, Toward a quantum-mechanical understanding of the high-resolution infrared spectrum of CH₅⁺, in: Contribution TA05, 61st International Symposium on Molecular Spectroscopy, Columbus, OH, USA, 2006.

^cOskar Asvany, Koichi M. T. Yamada, Sandra Brücken, Alexey Potapov, Stephan Schlemmer. Experimental ground-state combination differences of CH₅⁺. *Science*, 347(6228):1346–1349, 2015.

^dS. Brackertz, S. Schlemmer, O. Asvany, Searching for new symmetry species of CH₅⁺ – From lines to states without a model, *J. Mol. Spectrosc.* 342 (2017) 73–82.

^eH. Schmiedt, P. Jensen, S. Schlemmer, Rotation-vibration motion of extremely flexible molecules – the molecular superrotor, *Chem. Phys. Lett.* 672 (2017) 34–46.

^fX.-G. Wang, T. Carrington, Calculated rotation-bending energy levels of CH₅⁺ and a comparison with experiment, *J. Chem. Phys.* 144 (2016) 204304.