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, CH_5^+. 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 CH_5^+ 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].

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