

## Rovibrational and Hyperfine Structure of the Molecular Hydrogen Ion from Spectroscopy of Rydberg-Stark Manifolds

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$H_2^+$  is the simplest molecular three-body system, and is therefore of interest from a fundamental point of view. Specifically, precision measurements of rovibrational energies in this system can provide access to fundamental constants such as the proton-to-electron mass ratio or the proton charge radius, by comparison with theoretical results [1]. Because homonuclear isotopologues of molecular hydrogen have no permanent electric dipole, pure rotational and vibrational spectra cannot be measured. Instead, transitions to Rydberg series converging on different rovibrational states of the ion core can be driven in a multiphoton excitation scheme starting from the molecular ground state [2]. Extrapolation of Rydberg series yields the ionic level energies. In this work, we use a combination of high-precision laser spectroscopy and calculations of Rydberg-Stark manifolds including electron and nuclear spins to determine rovibrational and hyperfine intervals in  $H_2^+$  and  $HD^+$  at sub-MHz accuracy.

Experimentally, precise measurements of Rydberg states with a rovibrationally excited core are challenging because of line-broadening effects caused by autoionization. By applying electric fields, states of different values of orbital angular momentum  $l$  are mixed, which provides access to the non-penetrating states of high- $l$  character and therefore increases the lifetimes. Additionally, the high- $l$  states have vanishingly small quantum defects and form a nearly degenerate Stark manifold. Extrapolation to zero field yields the zero-quantum-defect positions [3], from which the ionization energy can be determined. By applying the zero-quantum-defect-method to states with the ion core in different rovibrationally excited states, energy differences between these ion core states are determined.

For rigorous comparison with the measurements, we present calculations of Stark manifolds including interactions involving electron and nuclear spins. In particular, because previous studies have shown that the calculated manifold positions are sensitive to the zero-field positions of high- $l$  states [3], we show how these positions can be accurately calculated with a simple polarization model [4] to which spin-orbit, spin-rotation and, if necessary, hyperfine interactions are added.

This contribution focuses on the determination of the fundamental vibrational and the spin-rotation intervals in  $H_2^+$  and the hyperfine splitting in the ground state of  $HD^+$ .

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