ROVIBRATIONAL AND HYPERFINE STRUCTURE OF THE MOLECULAR HYDROGEN ION FROM SPECTROSCOPY OF RYDBERG-STARK MANIFOLDS

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Precision measurements of rovibrational energies in H_2^+ 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 are nonpolar, pure rotational and vibrational spectra cannot be measured. Instead, transitions can be driven to Rydberg series converging on different rovibrational states of the ion core [2]. Extrapolation of Rydberg series yields the ionic level energies. We use a combination of precision spectroscopy and calculations of Rydberg-Stark manifolds including electron and nuclear spins to determine rovibrational and hyperfine intervals in H_2^+ and D_2^+ at sub-MHz accuracy.

Precise measurements of core-excited Rydberg states are challenging because of line-broadening effects caused by autoionization. By applying electric fields, states of different values of ℓ are mixed, which increases the non-penetrating character and thus the lifetimes. 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 this method to states with the ion core in different rovibrational states, their relative positions are determined.

We show how Stark manifolds including interactions involving electron and nuclear spins can be accurately calculated with a polarization model for the high-ℓ quantum defects [4] to which spin-orbit, spin-rotation and 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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