The fine and hyperfine structure of molecular hydrogen ions from spectroscopy of Rydberg states

Ioana Doran [1,†], **Leon Jeckel** [1], **Maximilian Beyer** [2], **Christian Jungen** [3], **Frédéric Merkt** [1]

[1]Institute of Molecular Physical Science, ETH Zürich, Switzerland
[2]Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands
[3]Université Paris-Saclay, Centre National de la Recherche Scientifique, Laboratoire Aimé Cotton, Orsay, France
†corresponding author's email: ioana.doran@phys.chem.ethz.ch

Precision measurements of spin-rovibrational energies in molecular hydrogen ions provide access to fundamental constants such as the proton-to-electron mass ratio or the proton charge radius, by comparison with theoretical results [1, 2, 3]. These ionic energy intervals can be determined precisely by Rydberg-series extrapolation [4, 5] of series converging to different spin-rovibrational states in the ion. Measurements of Rydberg-Stark manifolds at varying electric field strengths and comparison with precise calculations of the field-induced Stark shifts [6] enable the determination of the zero-quantum-defect positions $-R_{H_2}/n^2$, which yield precise ionization thresholds. The use of this procedure has recently been demonstrated in determining the fundamental vibrational interval of H_2^+ with sub-MHz uncertainty [7].

This contribution focuses on the extension of the zero-quantum-defect method to molecular hydrogen ions which have a fine or hyperfine structure. We present precision measurements and calculations of Stark manifolds in Rydberg states of molecular hydrogen including interactions involving the rotational angular momentum and the nuclear spin of the ion. Focusing on the spin-rotation splitting in para-H_2^+ ($v^+ = 1, N^+ = 2, I = 0$) and the hyperfine splitting in ortho-D_2^+ ($v^+ = 1, N^+ = 0, I = 0, 2$), we show that these calculations accurately describe the experimentally measured Rydberg-Stark manifolds quantitatively. Finally, the comparison between experiment and calculations is used to determine the hyperfine splitting in ortho-D_2^+ with an uncertainty in the low-kHz range.

References

[1] V. I. Korobov, L. Hilico, and J.-Ph. Karr, *Phys. Rev. Lett.* **118**, 233001 (2017).
[2] J.-Ph. Karr, and J. C. J. Koelemeij *Mol. Phys.* **121**, e2216081 (2023).
[3] S. Schiller, and J.-Ph. Karr, *Phys. Rev. A* **109**, 042825 (2024).
[4] G. Herzberg and Ch. Jungen, *J. Mol. Spectrosc.* **41**, 425 (1972).
[5] M. Beyer, N. Hölsch, J. Hussels, C. -F. Cheng, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, Ch. Jungen, and F. Merkt, *Phys. Rev. Lett.* **123**, 163002 (2019).
[6] N. Hölsch, I. Doran, M. Beyer, and F. Merkt, *J. Mol. Spectrosc.* **387**, 111648 (2022).
[7] I. Doran, N. Hölsch, M. Beyer, and F. Merkt, *Phys. Rev. Lett.* **132**, 073001(2024).