HIGH-RESOLUTION LASER SPECTROSCOPY OF THE RYDBERG STARK MANIFOLD IN H_2

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From the precise measurement of the ionization energy of H_2 its dissociation energy can be determined[a], which serves as a benchmark quantity for QED calculations[b]. The most precise determinations of the ionization energies of molecular hydrogen currently rely on the extrapolation of Rydberg series using multichannel quantum-defect theory (MQDT)[c].

Nonpenetrating high-ℓ states offer significant advantages for these extrapolations: they have small quantum defects and are much less perturbed by channel interactions than low-ℓ states. Their high polarisabilities are a disadvantage in zero-field measurements, but can be exploited to our advantage in Stark measurements. We show that the combination of a 3-photon excitation scheme with application of relatively weak electric fields (10 - 250 mV/cm) provides easy optical access to the linear Stark manifolds associated with near-degenerate high-ℓ states. We perform spectroscopy of the high-Rydberg Stark manifold with both continuous-wave millimeter-wave and near-infrared (NIR) radiation.

The manifold states are desirable as spectroscopic targets because their positions are less sensitive to errors in the quantum defects, a limiting factor in the determination of ionization energies by Rydberg series extrapolation. Extrapolating the linear Stark manifold to zero field yields accurate values of the zero-quantum-defect positions, given by $-\mathcal{R}_{\mathrm{H_2}}/n^2$ relative to the ionization thresholds. These positions constitute references for the respective $\ell = 3$ states and provide an assessment of multichannel-quantum-defect-theory calculations at a precision on the order of 100 kHz.

We show that this method can contribute to a one-order-of-magnitude improvement in the determination of ionization energies in molecular hydrogen and that, by using narrow-band NIR laser light, it can be extended beyond the ground state of para-H_2^+.

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[a] N. Hölsch, M. Beyer, E.J. Salumbides, K.S.E. Eikema, W. Ubachs, Ch. Jungen, and F. Merkt, Phys. Rev. Lett., 122(10), 103003 (2019)

[b] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki, Phys. Rev. Lett., 122(10), 103003 (2019)

[c] D. Sprecher, Ch. Jungen and F. Merkt, J. Chem. Phys. 140, 104303:1-18 (2014)