OBSERVATION OF HEAVY RYDBERG STATES IN H_2 AND HD

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The binding energies of the hydrogen atom are given by the Rydberg formula

$$E_n = -\frac{\mathcal{R}_\infty \mu / m_e}{(n-\delta)^2},$$

where the quantum defect δ vanishes in the case of a pure Coulomb potential.

Heavy Rydberg systems can be realized when the electron is replaced by an anion, which leads in the case of H^+H^- to an almost 1000 times larger Rydberg constant and to an infinite number of vibrational states. In the diabatic molecular basis, these ion-pair states are described by long-range Coulomb potentials with $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetry. In this basis, the level energies are described by an almost energy-independent, nonzero quantum defect, reflecting the finite size of H^-. Strong interactions at small internuclear distances lead to strong variation of δ with n.

Gerade [2] and ungerade [3] ion-pair states have been observed in H_2 with principal quantum numbers up to $n = 240$. The quantum defects in this range were found to vary with energy, indicating the inadequacy of a pure diabatic picture.

Spectra of ungerade heavy Rydberg states of H_2 with $n = 160 - 520$ showing that the quantum defect only becomes energy independent for $n > 350$ will be presented, supporting the description using a diabatic basis.

I will also present first observations of ion-pair states in HD, showing two series of heavy Rydberg states, H^+D^- and H^-D^+, which have different series limits. The experimental results will be discussed and compared with calculations using both an adiabatic and a diabatic basis.

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[3] R. C. Ekey, and E. F. McCormack, *Phys. Rev. A* **84**, 020501(R) (2011).