Cold molecules and high-resolution spectroscopy: Experiments on two-, three- and four-electron molecules

P. Jansen, S. Scheidegger, L. Semeria and F. Merkt, Physical Chemistry Laboratory, ETH Zurich, CH-8093 Zurich, Switzerland

The ability to manipulate the translational motion of atoms and molecules using radiation and inhomogeneous electric and magnetic fields offers new opportunities for precision atomic and molecular spectroscopy and collisional studies. The talk will present the results of recent experiments on cold samples of few-electron molecules generated by supersonic-beam-deceleration techniques. The use of these techniques to produce cold samples will be illustrated by experiments on molecular hydrogen and helium.

The interest of precision measurements on few-electron molecules results from the fact that the properties of these molecules can be calculated extremely precisely using *ab initio* quantum-chemical methods which include the evaluation of relativistic and quantum-electrodynamics contributions. The comparison of experimental and theoretical results in these systems thus enables rigorous tests of the theory, potentially only limited by the uncertainties in fundamental constants (1,2,3). The talk will focus on recent unpublished precision spectroscopic measurements of the Rydberg spectrum of He_2 using a cold, slow beam of metastable He_2 produced by multistage Zeeman deceleration (4). Rydberg-series extrapolation using multichannel quantum defect theory and parameters determined in Ref. (5) enabled the determination of the energy level structure of He_2^+ with unprecedented precision. The comparison with the latest *ab initio* calculations (6) provides information on the magnitude of relativistic and QED contributions to rovibrational energies in He_2^+. The advantage of using multistage Zeeman deceleration does not only result from the longer transit times of the decelerated molecules through the radiation field. The spin-rotational state selectivity of the Zeeman deceleration process can also be exploited to reduce the spectral congestion, minimize residual Doppler shifts, resolve the Rydberg series beyond $n = 200$, and assign their fine structures.

(1) *Theoretical transition frequencies beyond 0.1 ppb accuracy in H_2^+, HD^+, and antiprotonic helium*, V. I. Korobov, L. Hilico, and J.-Ph. Karr, Phys. Rev. A **89**, 032511 (2014)

(2) *Theoretical determination of the dissociation energy of molecular hydrogen*, K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, J. Chem. Theory Comput. **5**, 3039 (2009)

(3) *Towards measuring the ionisation and dissociation energies of molecular hydrogen with sub-MHz accuracy,* D. Sprecher and Ch. Jungen and W. Ubachs and F. Merkt, Faraday Disc. **150**, 51 (2011)

(4) *Slow and velocity-tunable beams of metastable He_2 by multistage Zeeman deceleration*, M. Motsch, P. Jansen, J. A. Agner, H. Schmutz, and F. Merkt, Phys. Rev. A **89**, 043420 (2014)

(5) *High-resolution spectroscopy and quantum-defect model for the gerade triplet np and nf Rydberg states of He_2*, D. Sprecher, J. Liu, T. Krähenmann, M. Schäfer, and F. Merkt, J. Chem. Phys. **140**, 064304 (2014)

(6*) Very accurate potential energy curve of the He_2^+ ion*, W.-C. Tung, M. Pavanello and L. Adamowicz, J. Chem. Phys. **136**, 104309 (2012)