HIGH-RESOLUTION SPECTROSCOPY OF np RYDBERG STATES OF He_2: 1. RYDBERG-STATE-RESOLVED THRESHOLD IONIZATION SPECTRA OF METASTABLE He_2

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A supersonic beam of metastable He_2^* a $^3\Sigma_u^+$ molecules was generated using a pulsed discharge at the exit of a pulsed valve prior to the gas expansion into vacuum.[a] Transitions to high np Rydberg states were recorded using photoionization and Rydberg-state-resolved threshold ionization spectroscopy.[b] Overview scans at moderate resolution (0.3 cm^{-1}) were obtained with ionization fields ranging from 1.3 to 133 V/cm, lowering the ionization thresholds by 5.5 and 55 cm^{-1}, respectively. Using a solid-state UV laser system[c] with a 20 MHz bandwidth, high-resolution spectra of Rydberg series with n up to 150 and with resolved fine structure of the initial He_2^* a $^3\Sigma_u^+$ (N'') state were recorded. The assignment of the observed Rydberg states is based on multichannel quantum defect theory calculations from a recent study[a] of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron and photoionization spectra of He_2 (see following talk). The extrapolation of the observed Rydberg series to their limits enabled the determination of the ionization energy of the a $^3\Sigma_u^+$ state and the rotational structure of the He_2^+ ion with a precision of better than 20 MHz.

[a]M. Raunhardt, M. Schäfer, N. Vanhaecke, F. Merkt, *J. Chem. Phys.* **128**, 164310 (2008).
[b]R. Seiler, U. Hollenstein, G. M. Greetham, F. Merkt, *Chem. Phys. Lett.* **346**, 201 (2001).
[c]R. Seiler, Th. A. Paul, M. Andrist, F. Merkt, *Rev. Sci. Instr.* **76**, 103103 (2005).