

MEASUREMENT OF ROTATIONAL LEVELS OF THE HOMONUCLEAR HELIUM DIMER CATION BY EXTRAPOLATION OF RYDBERG SERIES

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Metastable $^4\text{He}_2$ molecules [$a^3\Sigma_u^+$ ($v = 0, N = 1, 3, 5, 7$)] were produced in a supersonic expansion of neat helium atoms by striking a discharge at the orifice of a pulsed valve.^a Transitions to np Rydberg states (n up to 150) converging to the first rotational levels of the ground state of He_2^+ [$X^+ 2\Sigma_u^+$ ($v^+ = 0, N^+ = 1, 3, 5$)] were recorded at a precision better than 10^{-3} cm^{-1} using the technique of Rydberg-state-resolved threshold ionization spectroscopy.^b The observed Rydberg series reveal strong perturbations caused by rotational channel interactions and the appearance of the spectra is strongly influenced by weak electric fields present in the excitation region. The extrapolation of the Rydberg series to their limits using multichannel quantum defect theory enabled the determination of the rotational structure of the helium dimer cation and of quantum defect parameters for the corresponding ionization channels. These results represent a benchmark for *ab initio* calculations on three-electron systems.^{c,d}

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