

PRECISION MEASUREMENT OF THE IONIZATION ENERGY OF METASTABLE He₂

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Predicting the energy-level structure of molecules from first principles is one of the major goals and tasks of theoretical molecular physics and chemistry. Few-electron molecules are particularly attractive systems for comparison with experimental results because numerically “exact” predictions of molecular properties can in principle be obtained, i.e., predictions that are only limited in accuracy by the uncertainties of fundamental constants.

We present absolute-frequency measurements of transitions from rotational levels of the $a^3\Sigma_u^+$ ($v'' = 0$) metastable state of He₂ to np Rydberg states. The transition frequencies are determined by one-photon UV spectroscopy in slow molecular beams using a narrow-band laser system referenced to a frequency comb. The ionization energy of metastable He₂ and the rotational structure of the $X^+ 2\Sigma_u^+$ ($v^+ = 0$) ground state of He₂⁺ have been determined with unprecedented precision and accuracy using Rydberg-series extrapolation.