HIGH-RESOLUTION SPECTROSCOPY OF METASTABLE He\textsubscript{2} AND He\textsubscript{2}\textsuperscript{+}

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Having only three electrons, He\textsubscript{2}\textsuperscript{+} represents a system for which highly accurate \textit{ab initio} calculations are possible. The most accurate potential energy surface (PES) available in literature for He\textsubscript{2}\textsuperscript{+} in its X\textsuperscript{+} 2Σ\textsubscript{u}\textsuperscript{+} electronic ground state does not include relativistic or radiative corrections and treats nonadiabatic effects only partially\textsuperscript{1}. We have performed systematic studies\textsuperscript{2,3} of the rovibrational structure of He\textsubscript{2}\textsuperscript{+} using MQDT-assisted Rydberg-series extrapolation in cold molecular beams of He\textsubscript{2} in its metastable a3Σ\textsubscript{u}\textsuperscript{+} electronic state (He\textsubscript{2}\textsuperscript{*}). These measurements indicate a discrepancy between theory and experiment that rapidly increases with the rotational quantum number N\textsuperscript{+}, both for the rotational levels of the vibrational ground state and first excited vibrational state. Recently, Mátyus\textsuperscript{4} obtained more accurate values for the nonadiabatic corrections to the rovibrational levels of He\textsubscript{2}\textsuperscript{+} using R-dependent rotational and vibrational reduced masses for solving the nuclear Hamiltonian with the PES of Ref. 1. The work of Mátyus shows that part of the discrepancy in the rotational energies can indeed be attributed to the neglect of nonadiabatic effects, but the nonadiabatic corrections worsened the difference between theory and experiment for the vibrational energy. In addition to the gross rovibrational structure of He\textsubscript{2}\textsuperscript{+}, we determined the fine-structure intervals of the rotational levels of the vibrational ground state of He\textsubscript{2}\textsuperscript{+} from the observed fine-structure of high triplet np Rydberg states of He\textsubscript{2} and the rotational fine structure of He\textsubscript{2}\textsuperscript{*}\textsuperscript{5,6}. Effective fine-structure constants extracted from the observed splittings disagree with the isotopically scaled \textit{ab initio} result for \textsuperscript{3}He\textsuperscript{4}He\textsuperscript{+}\textsuperscript{7}. Our measurements may therefore serve as a benchmark to test and improve advanced calculations of three-electron molecules.

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