HIGH-RESOLUTION NEAR-INFRARED SPECTROSCOPY OF H_3^+ ABOVE THE BARRIER TO LINEARITY

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Twenty transitions from the fourth overtone and combination bands of H_3^+ ($5\nu_2^1$, $5\nu_2^3$, $5\nu_2^5$, $2\nu_1 + 2\nu_2^2$,...) have been observed. These transitions, which are more than 4600 times weaker than the fundamental band, occur in the near-infrared region and probe energy levels above the barrier to linearity (>10,000 cm^{-1}), the regime in which H_3^+ has enough energy to sample linear configurations. The detection of these transitions required the development of a high-resolution, high-sensitivity ($\Delta I/I \sim 1 \times 10^{-7}$) spectrometer based on a Ti:Sapphire laser and incorporating velocity modulation, heterodyne detection, noise subtraction, and multi-passing. Both pure hydrogen and He/H_2 plasmas were used to discriminate between H_3^+ and Rydberg transitions of H_2. The primary motivation for continuing the study of vibrational states beyond those spectroscopically probed to date[a] is to assist in the development of theoretical calculations of H_3^+. The measured rovibrational energy levels provide an experimental check of ab initio calculations in this region, which present a unique challenge to theorists[bcd].

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