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 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.

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Time required: 15 min
Session in which paper is recommended for presentation: 9

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*a* C. M. Lindsay and B. J. McCall, J. Mol. Spectrosc. 210, 60 (2001).
*d* J.K.G. Watson, personal communication, 1996.