SUPERSONICALLY COOLED MOLECULAR IONS IN A SLIT-JET DISCHARGE: HIGH-RESOLUTION INFRARED SPECTROSCOPY AND TUNNELING DYNAMICS OF HD_2O^+

FENG DONG, DAIRENE UY, SCOTT DAVIS, MARK CHILD, and DAVID J. NESBITT, *JILA, University of Colorado, Boulder, CO 80309*.

Jet-cooled high-resolution infrared spectra of partially deuterated hydronium ion, HD_2O^+ in the O-H stretch region (ν_3 band) are obtained for the first time, exploiting the high ion densities, long absorption path lengths, and concentration modulation capabilities of the slit jet discharge spectrometer. Least-square analysis with a Watson asymmetric top Hamiltonian yields rovibrational constants and provides high level tests of ab initio molecular structure predictions. Transitions out of both lower ($\nu_3^+ \leftarrow 0^+$) and upper ($\nu_3^- \leftarrow 0^-$) tunneling levels are observed, as well as transitions across the tunneling gap ($\nu_3^- \leftarrow 0^+$). The $\nu_3^- \leftarrow 0^+$ transitions in HD_2O^+ acquire oscillator strength by loss of C_{3v} symmetry and permit both ground (27.0318(72) cm^{-1}) and excited state (17.7612(54) cm^{-1}) tunneling splittings to be determined to spectroscopic precision from a single rovibrational band. The splittings and band origins calculated with recent high level ab initio 6D potential surface predictions for H_3O^+ and isotopomers [a] [b] are in very encouraging agreement with the current experimental results.

[a] X. C. Huang, S. Carter, and J. M. Bowman, J. Chem. Phys. 118 (12), 5431 (2003).
[b] T. Rajamaki, A. Miani, and L. Halonen, J. Chem. Phys. 118 (24), 10929 (2003).