FAR-INFRARED LASER VIBRATION-ROTATION- TUNNELING SPECTROSCOPY OF WATER CLUSTERS IN THE LIBRATIONAL BAND REGION

F. N. KEUTSCH, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; R. S. FELLERS, *Yahoo, 3420 Central Expressway, Santa Clara, CA 95051*; M. R. VIANT, *Department of Animal Sciences, University of California, Davis, CA 95616*; R. J. SAYKALLY, *Department of Chemistry, University of California, Berkeley, CA 94720*.

We report the first high resolution spectrum of a librational vibration for a water cluster.[a] Four parallel bands of $(H_2O)_3$ were measured between 510 and 525 cm^{-1} using diode laser VRT spectroscopy. The bands lie in the "librational band" region of liquid water and are assigned to the nondegenerate out of plane librational vibration. The observation of at least three distinct bands within 8 cm^{-1} originating in the vibrational ground state is explained by a dramatically increased splitting of the rovibrational levels relative to the ground state by bifurcation tunneling and is indicative of a greatly reduced barrier height in the excited state. This tunneling motion is of special significance, as it is the lowest energy pathway for breaking and reforming of hydrogen bonds, a salient aspect of liquid water dynamics.

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