THE CURIOUS CASE OF PYRIDINE - WATER

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The rotational spectrum of the pyridine$\cdots$water complex has been observed in the 2-18 GHz region using chirped-pulse and cavity Fourier transform microwave spectroscopy. The water is hydrogen bonded to the nitrogen, as expected, but the hydrogen bond is bent, with the oxygen tilted toward either of the ortho hydrogens of the pyridine. This gives rise to a pair of equivalent configurations and the possibility of a tunneling motion involving an in-plane rocking of the water. DFT calculations support this view. Experimentally, a pair of states with severely perturbed rotational structure has been identified and the spectra assigned. Analysis of the perturbations in the *a*-type (pure rotation) spectra has enabled an accurate determination of the tunneling splitting, which has been confirmed by direct observation of *b*-type (rotation-tunneling) transitions. A simultaneous fit of the *a*- and *b*- type transitions gives the most accurate value of the tunneling splitting. Results for the H_2O, D_2O, and D-bound HOD complexes will be presented. The tunneling splittings are as follows: H_2O-pyridine (10402.9 MHz), HOD-pyridine (12513.4 MHz, determined only from perturbation analysis), and D_2O-pyridine (13582.3 MHz). Curiously, the tunneling splitting increases with increased deuteration. Additional small splittings have been observed in some transitions, indicating the possibility of further internal dynamics. This system offers an interesting test case for theoretical treatments of large amplitude motion.