ROTATIONAL SPECTRA OF HYDROGEN-BONDED COMPLEXES BETWEEN FORMIC ACID AND WATER

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Rotational transitions of several complexes between formic acid and water have been observed with a pulsed nozzle Fourier transform microwave spectrometer. The rotational transitions have been assigned with the help of their Stark effect and of microwave-microwave double resonance experiments. They have been grouped into three different sets of transitions corresponding to three different complexes. Three rotational constants and some centrifugal distortion constants have been fitted for each complex. The μ_a- and μ_b-components of the permanent electric dipole moments have been determined from quantitative Stark measurements for all three complexes. The dipole moments and the small but negative inertia defects have suggested an essentially planar structure for all complexes. Models of hydrogen-bonded complexes that are compatible with the observed rotational constants have been constructed. The assigned transitions have been attributed to formic acid–water forming a six-membered ring with two hydrogen bonds, formic acid–$(\text{water})_2$ forming an eight-membered ring with three hydrogen bonds and $(\text{formic acid})_2$–water forming a ten-membered ring with three hydrogen bonds. The model structures are consistent with those from *ab initio* calculations.