MICROWAVE SPECTROSCOPY AND PROTON TRANSFER DYNAMICS IN THE FORMIC ACID-ACETIC ACID DIMER

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The rotational spectrum of the doubly hydrogen-bonded *hetero* dimer formed between formic acid and acetic acid has been recorded between 4 and 18 GHz using a pulsed-nozzle Fourier transform microwave spectrometer. Each rigid-molecule rotational transition is split into four as a result of two concurrent tunnelling motions, one being proton transfer between the two acid molecules, and the other the torsion/rotation of the methyl group within the acetic acid.

We present a full assignment of the spectrum for $J = 1$ to $J = 7$ for these four torsion/tunnelling states. Spectra have been observed for the main isotopic species [a], with deuterium substitution at the C of the formic acid and all ^{13}C species in natural abundance, The observed transitions are fitted to within a few kilohertz using a molecule-fixed effective rotational Hamiltonian for the separate *A* and *E* vibrational species of the G_{12} permutation-inversion group which is applicable to this complex. To reduce the effects of internal angular momentum, a non-principal axis system is used throughout. Interpretation of the internal motion uses an internal-vibration and overall rotation scheme, and full sets of rotational and centrifugal distortion constants are determined.

The proton tunnelling rates and the internal angular momentum of the methyl group in the *E* states is interpreted in terms of a dynamical model which involves coupled proton transfer and internal rotation. The resulting potential energy surface not only describes these internal motions, but can also explain the observed shifts in rotational constants between *A* and *E* species, and the deviations of the tunnelling frequencies from the expected 2:1 ratio. It also permits the determination of spectral constants free from the contamination effects of the internal dynamics.

[a] M.C.D. Tayler, B. Ouyang and B.J. Howard, *J. Chem. Phys.*, **134**, 054316 (2011).