DOING THE LIMBO WITH A LOW BARRIER: HYDROGEN BONDING AND PROTON TRANSFER IN HYDROXYFORMYLFULVENE

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Model compounds continue to play crucial roles for elucidating the ubiquitous phenomena of hydrogen bonding and proton transfer, often yielding invaluable insights into kindred processes taking place in substantially larger species. The symmetric double-minimum topography that characterizes the potential-energy landscape for an important subset of these systems allows unambiguous signatures of molecular dynamics (in the form of tunneling-induced bifurcations) to be extracted directly from spectral measurements. As a relatively unexplored member of this class, 6-hydroxy-2-formylfulvene (HFF) contains an intramolecular O–H···O interaction that has participating atoms from the hydroxylic (donor) and ketonic (acceptor) moieties closely spaced in a quasi-linear configuration. This unusual arrangement suggests proton transduction to occur with minimal encumbrance, possibly leading to a pronounced dislocation of the shuttling hydron commensurate with the concepts of low-barrier hydrogen bonding (which are distinguished by great strength, short distance, and vanishingly small potential barriers). A variety of spectroscopic probes built primarily upon the techniques of laser-induced fluorescence and dispersed fluorescence have been enlisted to acquire the first vibronically resolved information reported for the ground [$\tilde{X}^1A_1$] and lowest-lying singlet excited [$\tilde{A}^1B_2$ ($\pi^*\pi$)] electronic manifolds of HFF entrained in a cold supersonic free-jet expansion. These experimental findings will be discussed and compared to those obtained for related proton-transfer systems, with complimentary quantum-chemical calculations serving to unravel the unique bonding motifs and reactive pathways inherent to HFF.