Our fundamental understanding of synergistic hydrogen-bonding and proton-transfer phenomena has been advanced immensely by studies of model systems in which the coherent transduction of hydrons is mediated by two degenerate equilibrium configurations that are isolated from one another by a potential barrier of substantial height. This topography advantageously affords unambiguous signatures for the underlying state-resolved dynamics in the form of tunneling-induced spectral bifurcations, the magnitudes of which encode both the overall efficacy and the detailed mechanism of the unimolecular transformation. As a prototypical member of this class of compounds, 6-hydroxy-2-formylfulvene (HFF) supports an unusual quasi-linear O–H⋯O ↔ O⋯H–O reaction coordinate that presents a minimal impediment to proton migration – a situation commensurate with the concepts of low-barrier hydrogen bonding (which are characterized by great strength, short distance, and a vanishingly small barrier for hydron migration). A variety of fluorescence-based, laser-spectroscopic probes have been deployed in a cold supersonic free-jet expansion to explore the vibrational landscape and anomalously large tunneling-induced shifts that dominate the $\tilde{X}^1A_1$ potential-energy surface of HFF, thus revealing the most rapid proton tunneling ever reported for a molecular ground state ($\tau_{pt} \leq 120$fs). The surprising efficiency of such tunneling-mediated processes stems from proximity of the zero-point level to the barrier crest and produces a dramatic alteration in the canonical pattern of vibrational features that reflects, in part, the subtle transition from quantum-mechanical barrier penetration to classical over-the-barrier dynamics. The ultrafast proton-transfer regime that characterizes the $\tilde{X}^1A_1$ manifold will be juxtaposed against analogous findings for the lowest-lying singlet excited state $\tilde{A}^1B_2 (\pi^* \leftrightarrow \pi)$, where a marked change in the nature of the reaction coordinate leads to the near-complete quenching of proton transfer. Experimental results, as well as complementary quantum-chemical analyses, will be discussed and contrasted with those obtained for related hydron-migration systems in an effort to highlight the unique bonding motifs and reaction propensities evinced by HFF.