TROPOLONE COMPLEXES FORMED WITH AMPHOTERIC LIGANDS: STRUCTURE AND DYNAMICS AS VIEWED ACROSS THE VIBRONIC LANDSCAPE

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Owing to the presence of a finite potential barrier that adjoins hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen atom centers, tropolone (TrOH) long has served as a model system for the investigation of coherent (symmetrical) proton-transfer events. Hydrogen-bound complexes formed by docking amphoteric species onto the TrOH substrate, such as those involving formic acid [TrOH-(FA)$_n$] and other simultaneous donor-acceptor ligands, have been generated under supersonic free-jet expansion conditions. For binary adducts (n=1), quantum-chemical calculations predict two nearly degenerate isomers that can be labeled as external (ligand attached to the seven-membered aromatic ring) and internal (ligand bound to the $\mathrm{O{-}H\cdots O}$ reaction site), where the latter cleft-bound form offers the tantalizing possibility of undergoing a double proton-transfer process. A variety of spectroscopic probes build around the intense $\tilde{A}^1\mathrm{B}_2 - \tilde{\mathrm{X}}^1\mathrm{A}_1$ ($\pi^* \leftarrow \pi$) near-ultraviolet absorption feature of bare tropolone have been enlisted to elucidate the binding motifs and reaction pathways in complexes containing one or more amphoteric ligands, including vibrationally resolved schemes based upon laser-induced fluorescence (LIF), dispersed fluorescence (DF), and fluorescence hole-burning (FHB) methods. Structural and dynamical information gleaned from these experiments will be discussed in light of complementary *ab initio* calculations.