A COMPUTATIONAL STUDY OF DOUBLE PROTON TRANSFER IN THE TROPOLONE-HF COMPLEX

LORI A. BURNS, DANIEL MURDOCK, and PATRICK H. VACCARO, *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107.*

Many processes of chemical and biological importance depend critically upon the cooperative action of several hydrogen bonds, as do related multiple proton-transfer (MPT) events. The distinct hydrons participating in MPT pathways interact not only with restricted skeletal motions of the molecular framework, but also with the large-amplitude displacements of other shuttling atoms. Consequently, the dynamics exhibited by these processes are expected to be more complex and varied than those of their single-proton counterparts, such as the prototypical tropolone (TrOH) system. This talk will explore the binary cleft-complex (TrOH-HF) formed by binding HF into the tropolone reaction site, a model adduct for probing the sequential versus concerted nature of double proton-transfer processes. The ground electronic state of TrOH-HF shares many distinguishing features inherent to bare TrOH, including a symmetric double-minimum potential well in which two stable and equivalent structures of planar C_s symmetry are separated by a C_{2v} transition state. Our *ab initio* studies have utilized the coupled cluster ansatz (CCSD/EOM–CCSD) in conjunction with extensive correlation-consistent basis sets to examine the $\tilde{X}\,^1\mathrm{A}_1$ and $\tilde{A}\,^1\mathrm{B}_2$ electronic manifolds. The synchronous double proton-transfer reaction in TrOH-HF is predicted to exhibit a barrier of $2307.2\,\mathrm{cm}^{-1}$ height, representing a 30% drop from the analogous value for TrOH, $3294.2\,\mathrm{cm}^{-1}$. Redistribution of charge density upon $\pi^* \leftarrow \pi$ electronic excitation transforms the potential energy surface, yielding diminished barriers for both the bare ($1135.8\,\mathrm{cm}^{-1}$) and complexed ($945.8\,\mathrm{cm}^{-1}$) species. Intriguingly, the pathway for double proton transfer in electronically-excited TrOH-HF shows evidence of nonplanarity, including the the presence of a twisted (C_2) transition-state geometry in which the lone imaginary frequency combines concerted O–H/F–H stretching motions with a geared rotation of the reaction site. The potential energy landscapes of TrOH and TrOH-HF, as well as the underlying nature of the vibrationally-mediated hydron migration process, will be discussed within the framework of the encompassing G_4 molecular symmetry group.