PHENYLACETYLENE-FORMIC ACID COMPLEXES – A RICH LANDSCAPE OF HYDROGEN BONDED HETERODIMERS STUDIED USING MATRIX ISOLATION INFRARED SPECTROSCOPY AND *AB INITIO* COMPUTATIONS

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Abstract:

Phenylacetylene (PhAc) and Formic Acid (FA) are both polyfunctional molecules keeping hydrogen bonding interactions in perspective; i.e. both can serve as proton acceptors and/ or proton donors. PhAc has acetylenic and phenyl π systems, which can serve as proton acceptors, while the ≡C-H group can act as a proton donor. Likewise, FA also has both proton donor and acceptor sites. In addition, FA exists in two conformers-anti and syn, the hydroxyl hydrogen being located on the same or opposite side of the hydrogen attached to carbonyl carbon. Consequently a number of isomers are possible for the hydrogen bonded PhAc-FA complexes, and the heterodimer potential surface therefore offers a rich landscape. While this situation is a theorists delight, it is an experimentalists' nightmare.

The PhAc-FA system was studied using matrix isolation infrared spectroscopy and *ab initio* computations. Computations were performed employing MP2 and M06-2X methods, with 6-311++G (d,p) and aug-cc-pVDZ basis sets. Interaction energies of various complexes were also calculated at MP2/CBS and CCSD(T)/CBS limit. Stabilization energies of the different isomers of PhAc-FA complexes ranged from 1 to 7 kcal/mol. In fact computations indicated more than 10 hydrogen bonded isomeric structures for the PhAc-FA system, involving one or more C-H···π, C-H···O and O-H···π contacts. Amongst all the complexes, an isomer with an O-H···π interaction, in which FA acts as proton donor through O-H moiety to the π cloud of PhAc was indicated to be the global minimum.

Experimentally, a structure involving an O-H···π interaction, was observed in both N_2 and Ar matrix, identified by a red shift of ~111 cm^{-1}(in N_2) and 149 cm^{-1} (in Ar) in the O-H stretching frequency of FA, which was in agreement with computed global minimum. Experiments with phenylacetylene deuterated at the acetylenic hydrogen ($PhAc_D$) were also performed, to confirm the above observation, through the isotopic effect. AIM, EDA and NBO analysis were performed to explore the nature, physical origin and the strength of the noncovalent interactions. Clearly, the PhAc-FA system presents a challenging and interesting study, with one of the richest landscapes for hydrogen bonding complexes. The talk will highlight the results of this work.