PROTON TUNNELING IN BASE PAIR ANALOGS: UNDERSTANDING THE MECHANISMS BEHIND A DOUBLE-PROTON TRANSFER[a]

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The rotationally resolved electronic spectrum of a tautomeric base pair analog, the 2-hydroxypyridine/2-pyridone dimer in the gas phase has been obtained and interpreted. Using theoretical monomer structures, a doubly hydrogen bonded structure is proposed, in which the NH-N distance is similar to those found elsewhere, but the OH-O distance is considerably smaller. In addition, a tunneling splitting is observed corresponding to a double-proton transfer across these two hydrogen bonds. Analysis of the partially and doubly-deuterated dimer spectra reveals that the O-H and N-H stretches play different roles in the tunneling process. Possible theoretical interpretations are discussed.

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