

Electrostatic and non-electrostatic contributions to hydrogen bonding and proton transfer in solution phase

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A combined methodology of semiempirical density functional (DFT) and Hartree-Fock (HF) theories is used to analyze the solution-phase proton-transfer (PT) process in the $\text{H}_2\text{O}\cdots\text{HX}$ ($X = \text{F}, \text{Cl}, \text{and OH}$) model systems. Gas-phase PT, hydrogen bonding, ion-pairing, dissociation, and solvent effect are considered as the contributing factors to the solution PT reaction. The H-bonded and ion-pair structures are determined from the proton-transfer potential (PTP) profiles and full geometry optimization, using the Amsterdam density functional (ADF) code. These structures are then used as input to the semiempirical SCRF/CNDO method that incorporates solvent effects. The semiempirical SCRF gas-phase results qualitatively reproduce the experimental trend for the gas-phase proton affinities (PA) ($\text{OH}^- > \text{F}^- > \text{Cl}^-$). The solution-phase results correctly explain the strong acid character of HCl ($\text{pK}_a < 0$) and the weak dissociation of HF ($\text{pK}_a > 0$) in water. © 1996 American Chemical Society.