

MOLECULAR ORBITAL STUDY OF THE HYDRATED CLUSTERS OF STRONG ACIDS WITH WATER MOLECULES

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The molecular structures and vibrational frequencies of the hydrated clusters of the strong acids, $\text{HCl}\bullet(\text{H}_2\text{O})_n$ and $\text{H}_2\text{SO}_4\bullet(\text{H}_2\text{O})_n$; $n=1\sim 5$, are examined by employing the density functional molecular orbital method. When the number of water molecules is small, the hydrated clusters take the hydrogen-bonded structures without proton transfer. In the cases of $n\geq 4$, the proton transferred forms become dominant and there are many isomeric forms for both the direct ion-pair $\text{X}^-\bullet\text{H}_3\text{O}^+\bullet(\text{H}_2\text{O})_{n-1}$, and indirect ion-pair $\text{X}^-\bullet(\text{H}_2\text{O})_{n-1}\bullet\text{H}_3\text{O}^+$ structures, where $\text{X}=\text{Cl}, \text{HSO}_4$. The calculated IR spectra of the stable clusters clearly indicate the large red-shifts of the stretching frequencies of the H-Cl and the O-H bond of H_2SO_4 . The difference of the hydrated clusters of HCl, H_2SO_4 , and HF is also discussed.