PSEUDO JAHN–TELLER ORIGIN OF THE PROTON TUNNELING IN ZUNDEL CATION CONTAINING WATER CLUSTERS

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S u m m a r y

The pseudo Jahn–Teller (PJT) origin of the proton transfer barrier in the Zundel cation at different O-O distances and in an $H_5O_2^+(H_2O)_4$ cluster is revealed by means of *ab initio* calculations of their electronic structures and the adiabatic potential energy curves. The vibronic constants in this approach were estimated by fitting the *ab initio* calculated adiabatic potential to its analytical expression. It is shown also that the high-symmetry nuclear configurations of proton-centered water clusters of the type $H^+(H_2O)_n$ $(n = 6, 4, 3)$ are unstable with respect to the low-symmetry nuclear distortions leading to forming the dihydronium cation $H_5O_2^+$ and the appropriate number of water molecules: $H_{2n+1}O_n^+ \rightarrow (n-2)H_2O + H_5O_2^+$. The reason for this instability and the subsequent decay is the PJT coupling between the ground and excited electronic states.