Abstract
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Hydrogen Bond Network Rearrangement Dynamics in Water Clusters: Dramatic Effects of Librational Excitation on Hydrogen Bond Tunneling Rates

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Theoretical studies of the hydrogen bond network rearrangement (HBNR) dynamics in liquid water have indicated that librational motions initiate the HB breaking/formation processes. We present the results of using a simple time evolution method to extract and compare the hydrogen bond tunneling lifetimes for the water dimer, trimer, pentamer and hexamer from the experimentally measured tunneling splittings in the ground and singly excited intermolecular vibrational states. We find that that the specific nature of the intermolecular vibrational excitation does not significantly influence the tunneling lifetime of the dimer, but that excitations of a librational vibration dramatically decrease the water trimer, pentamer, or hexamer lifetimes. Hence, observing and quantifying the enhanced hydrogen bond breaking dynamics for these types of vibrations in water clusters serves as support for theoretical predictions. The specific enhancement of tunneling in larger clusters relative to the dimer also indicates that hydrogen bond cooperativity is a vital element of these dynamics.

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