VIBRATION-ROTATION-TUNNELING-SPECTROSCOPY OF $(H_2O)_4$ AND $(H_2O)_5$: THE DRAMATIC EFFECT OF SYMMETRY ON HYDROGEN BOND TUNNELING DYNAMICS

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Terahertz VRT-spectra of small water clusters show splittings of the energy levels that can be explained by large amplitude vibrations and hydrogen bond rearrangement dynamics [a].

For example, the cyclic water pentamer has an asymmetric equilibrium structure, and the effects of both the facile torsional motion of the free hydrogens (flipping) and the exchange of the free and bound hydrogen on one water molecule (bifurcation tunneling motion) are observed in the VRT spectra [b].

In contrast, the cyclic water tetramer has an oblate symmetric top equilibrium structure before vibrational averaging [a]. Whereas the flipping of one free hydrogen leads to a very large tunneling splitting in the water trimer and pentamer, there is no such facile process for the water tetramer. The high symmetry of the water tetramer requires a higher degree of cooperativity, which results in a far smaller number of facile tunneling motions. Although previous spectra and theoretical results indicate a tunneling process involving all four free hydrogens, the pathway is still unknown. A recently measured vibrational band at 4 THz allows us to gain new insight into the possible significant pathways.

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[b] M. G. Brown, F. N. Keutsch, R. J. Saykally, J. Chem. Phys. 1998 109, 9645.