CONCERTED BREAKING OF TWO HYDROGEN BONDS IN WATER HEXAMER PRISM REVEALED FROM BROADBAND ROTATIONAL SPECTROSCOPY

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Over the past few years, we have used $H_2^{18}O$ water substitution to determine the structures of water clusters by molecular rotational spectroscopy. In the case of the water hexamer, the energy difference between the cage and prism structures is calculated to be about 0.1 kcal/mol and this energy difference is of the order of the zero-point energy variation between the isomers. Using rotational spectroscopy we provided experimental evidence for three isomers, i.e, cage, prism and book and established their relative energy ordering.[a] In the special case of the prism hexamer, cluster dynamics causes measurable splitting in rotational transitions resulting from tunneling between discernible equivalent minima. Multiple isotopic substitution measurements involving all 64 possible isotopologues of the water hexamer prism $(H_2^{18}O)_n(H_2^{16}O)_{6-n}$ were performed in order to identify the water molecules involved in the tunneling motion. The analysis of these tunneling-rotation spectra suggests that there are two distinct tunneling paths that involve concerted motion of two water molecules, implying a prototype scenario involving the breaking of two hydrogen bonds.[b]

[a] C. Pérez, et al, *Science.* **2012**, *336* 897-901

[b] J. O. Richardson et al, *Science.* **2016**, *in press*