The water hexamer is the first cluster size where three dimensional structures become the most stable. For cluster sizes up to the water decamer, the hexamer is unique because there are three low-lying isomers with distinct oxygen framework geometries that can be observed in pulsed molecular beams: the prism, cage, and book. Each structure has a different number of hydrogen bonds (prism: 9, cage: 8, book: 7). The prediction of the lowest energy form by different water potentials has become a benchmark in computational studies of water clusters. The experimental determination that the cage is the lowest energy form was presented by our group in 2012 using the population changes that occur when different carrier gases are used in the molecular beam expansion. Recently, it has been proposed by Babin and Paesani that the relative energy ordering of these isomers might be useful for testing the ability of theory to include zero-point energy effects. Their calculations suggested that the prism might become the lowest energy isomer in the fully deuterated water hexamer. At the simplest level, this can explained by the fact that the prism has the most hydrogen bonds and would, therefore, experience the most energy lowering upon isotopic substitution. Broadband rotational spectroscopy in a pulsed supersonic expansion has been used to study the cage, prism and book isomers of deuterated water hexamer. These data, in conjunction with new computational advances, quantify the changes in the oxygen framework structure respect to the normal water hexamers. Moreover, by using different gases in the expansion we have established that the prism isomer becomes the minimum energy structure as suggested by Babin and Paesani.

The water hexamer is the smallest water cluster to support low-energy structures with branched three-dimensional hydrogen-bond networks, rather than cyclic two-dimensional topologies. Here we report measurements of splitting patterns in rotational transitions of the water hexamer prism, and we used quantum simulations to show that they result from geared and antigeared rotations of a pair of water molecules. Unlike previously reported tunneling motions in water clusters, the geared motion involves the concerted breaking of two hydrogen bonds. Similar types of motion may be feasible in interfaces. A broadband Fourier transform microwave spectrometer based on chirped pulse excitation. Rev. Sci. Energies of the water hexamer conformers. In this work, we definitively assign the ground state structure of the ethanol–water dimer to a water-donor structure, with ethanol in the gauche conformation. The spectrum of the ethanol–water dimer was collected using the Caltech chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer between 8–18 GHz. The mixed dimer was prepared by loading water into a reservoir pulsed valve, and flowing a backing gas (argon) over a separate external reservoir containing ethanol. The mixture of ethanol, water, and 2 atmospheres of backing gas (typically Ar or He) was supersonically expanded into a vacuum chamber at 10−5 Torr with a pulse repetition rate of 5 Hz.