IDENTIFICATION OF THE CAGE, PRISM, AND BOOK ISOMERS OF WATER HEXAMER AND THE PREDICTED LOWEST ENERGY HEPTAMER AND NONAMER CLUSTERS BY BROADBAND ROTATIONAL SPECTROSCOPY

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The water hexamer is predicted to be the smallest water cluster with a three-dimensional hydrogen bonding network as its minimum energy structure. Calculations indicate that there are several possible low-energy isomers, with different levels of theory identifying different isomers as the global minimum. Previous experimental work has provided evidence for the cage, book, and cyclic isomers but no experiment has identified multiple coexisting structures. Using broadband rotational spectroscopy in pulsed supersonic expansion these three isomers have now been unambiguously identified and their oxygen framework structures determined by means of $H_2^{18}O$ substitution. Relative isomer populations at different expansion conditions establish that the cage isomer is the minimum energy structure. The comparison of experimental and theoretical rotational constants shows that significant improvement in the agreement is achieved when vibrationally averaged (0 K) theoretical structures are used. For the water hexamer isomers, only the prism shows effects from tunneling associated with the rearrangement of the H-bond network. This tunneling is quenched upon the incorporation of a single $H_2{}^{18}O$ monomer into the prism cluster. Rotational spectra consistent with predictions for the lowest energy heptamer and nonamer structures have also been identified and the structure of the heptamer oxygen atom framework has also been determined using $H_2{}^{18}O$ substitution.